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CHEMICAL EXAMINATION OF AETHUSA CYNAPIUM.[1]

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Aethusa Cynapium, Linn, or "Fool's Parsley," known also as the "Lesser Hemlock," in French as "La petite Ciguë," in Italian as "Cicuta minore," and in German as the "Kleiner Schierling," is a well-known annual garden weed, which is indigenous to Europe and Northern Asia, and is the only representative of the genus. The generic name is stated to be derived from the Greek αἴθω σσω, to make warm, on account of the acrid taste of the plant.

In all the botanical works that have been consulted which give a description of the *Aethusa*, as also in works on toxicology and many other publications, it is regarded as possessing poisonous properties. Numerous cases of poisoning have in fact been attributed to it, and in most of these it appears to have been mistaken for the common garden parsley. On the other hand, the investigations of the plant which have hitherto been recorded, both chemical and physiological, have led to widely differing conclusions respecting its constituents and properties, and thus its reputed poisonous action has alternately been affirmed and denied. It is evidently on account of the recognition or suspicion of its harmful character that the *Aethusa* has received such ex-

[1] Presented, in abstract, at the Congress of Chemistry and Pharmacy, held at Liége, Belgium, July, 1905.

tended consideration in botanical and medical literature, and as some of the earlier observations concerning it are of interest and importance in connection with the present investigation, they may, so far as practicable, be briefly reviewed.

In the "Gardener's and Botanist's Dictionary," by Philip Miller, F.R.S., with additions by Thomas Martyn, F.R.S., Vol. I, Part I, London, 1807, the following reference occurs: "*Aethusa Cynapium*, Fool's Parsley, called also Lesser Hemlock, is a very common weed in kitchen gardens, and is in a slight degree poisonous." It is also remarked that this plant can only be confounded with true parsley and with chervil (*Anthriscus*) when in a very young state, and that "even then the leaves may be observed to have a different form, a darker hue, and, on being bruised, to emit in a slight degree a disagreeable venomous smell. Most cattle eat it, but it is said to be noxious to geese."

Stephenson and Churchhill in their "Medical Botany," Vol. I, London, 1831, give a detailed account of the *Aethusa*, and record several cases of poisoning attributed to it. They refer to its noxious qualities, and state that the leaves, when bruised, have a disagreeable odor. An instance is also cited by them where it had inadvertently been used as a medicine in place of hemlock (*Conium maculatum*) and with alarming results, thus indicating that at that early date the *Aethusa* was regarded as the more highly poisonous of these plants.

In Lindley and Moore's "Treasury of Botany," Vol. I, p. 26, the following is noted under *Aethusa*. "Its flavor and odor are unpleasant, and the seeds are very nauseous. The whole plant is said to be poisonous, and there are instances on record of persons having been made ill by eating it, even in the small quantities in which it is likely to have been present when mixed with parsley."

In Bentley and Trimen's "Medicinal Plants," Vol. II, No. 125, the *Aethusa* is noticed at considerable length. The following is there stated: "This plant is not official in any Pharmacopoeia, neither has it ever been used in regular medical practice; but it is introduced into the present work like *Oenanthe crocata* and *Cicuta virosa* on account of its poisonous properties; and hence, being a common indigenous plant, it ought to be well-known to medical practitioners and pharmacists. Its chief resemblance to parsley is in its leaves, but those of Fool's Parsley are more acute, of a

darker green color, and when bruised they emit a peculiar, disagreeable odor, which is altogether different from the smell of parsley. The whole plant possesses poisonous properties, but it does not appear to be of so virulent a nature as *Oenanthe crocata* and *Cicuta virosa*, for although there are several cases of poisoning by it, only two appear to have terminated fatally. In referring to the statement by Miller[1] that "most cattle eat it," the authors remark that "in all recorded experiments with it on animals, it has had poisonous effects"

In Gray's "Manual of Botany of the Northern United States," sixth edition, p. 205, the author describes *Aethusa Cynapium* as "a fetid, poisonous European herb"

In "Luerssen's Medicinisch-Pharmaceutische Botanik," 1882, Bd. II, p. 769, the author states, regarding *Aethusa*, that "this poisonous plant may be distinguished from parsley, which it resembles in a young state, not only by the described botanical characters, but by lacking the peculiar odor of the latter plant."

In Orfila's "Treatise on Mineral, Vegetable, and Animal Poisons," second edition, Vol. II, pp. 249–250, London, 1818, reference is made to the poisonous action of *Aethusa*, and this is also the case in the work "On Poisons," by Taylor, p. 758, London, 1848, although in the third edition of the latter work the conclusions of Harley, as noted below, are accepted as final

Dr. John Harley[2] made a number of physiological tests, by administering to a child and to adult persons the expressed juice of both immature and mature plants, collected in different counties in England, and, as no effects were observed, he came to the conclusion that the *Aethusa* is absolutely free from the noxious properties attributed to it. He states that "It is pleasant to the sight, smell and taste, and, in the absence of the more fragrant and succulent plants, might well be used as a pot-herb or a salad." It was stated, furthermore, that "these conclusions are independent both of locality and season, and that the only influence which these conditions have on Fool's Parsley, as on hemlock, is to increase or diminish its succulency."

In connection with the views expressed by Dr. Harley, it is of interest to note that so recently as 1904 a case of severe poisoning by Fool's Parsley was reported.[3] The plant, recognized as

[1] *Loc. cit.*

[2] "Year Book of Pharmacy," 1876, p. 200, and *Pharm. Journ.*, 1880, **11**, p. 437.

[3] *British Medical Journal*, July 16, 1904, p. 124.

Aethusa Cynapium, was stated to have been gathered in the kitchen garden and eaten in considerable quantity, but the symptoms of poisoning were not manifested until some twenty-four hours after ingestion. By the use of morphine (for the pain) and stimulants, a speedy recovery was effected. (Compare also Dr. Scott Sugdein, in the *Lancet*, July 7, 1888.)

Although the *Aethusa* appears never to have been subjected to a complete chemical examination, the statements that have been recorded respecting its constituents are quite as divergent as those pertaining to its physiological action. The earliest observation known to us in this connection is contained in the *Archiv des Apotheker Vereins im nördlichen Teutchland*, **24**, 251, Lemgo, 1828, from Kastner's *Archiv.*, **11**, 144, and is as follows: "The *Aethusa Cynapium*, which is often confused with parsley, contains, according to Professor Ficinus, an alkaloid, *cynapine*, which crystallizes in rhombic prisms, and is soluble in water and alcohol, but not in ether; the sulphate crystallizes in prisms."

Walz,[1] by the direct distillation of the ripe fruit of the *Aethusa*, and also by distillation of an alcoholic extract of the fruit with lime, obtained an alkaline distillate, which, when neutralized with sulphuric acid and extracted with ether-alcohol, left a residue of ammonium sulphate, while a substance dissolved which formed a brown, salt-like mass. The latter, when heated with a solution of caustic potash, gave a strongly alkaline distillate, having an odor resembling that of both coniine and nicotine, which afforded precipitates with various metallic salts and with the usual alkaloid reagents. He therefore concluded that the fruit of *Aethusa* contains "a volatile base, very similar in odor and chemical behavior to coniine, and probably identical with it." As minor constituents, he also observed the presence of an essential oil, a fatty oil, and two resins, one of which was soluble and the other insoluble in ether.

Bernhardt,[2] by the distillation of the fruit of *Aethusa* with milk of lime, obtained a reddish yellow liquid, floating like oil in the aqueous distillate. Both the oily liquid, in alcoholic solution, and the aqueous distillate possessed a strongly alkaline reaction, and an exceedingly penetrating, offensive odor, resembling that of rancid fish oil. The oily substance was found to contain nitrogen, and was therefore regarded as a volatile alkaloid. It

[1] *Neues Jahrbuch für Pharmacie*, **12**, 351–356 (1859).

[2] *Archiv. Pharm.* [3], **16**, 117, Halle, 1880, also *Year Book of Pharmacy*, 1880, p. 186.

was also stated that the odor of the substance, when in a concentrated state, caused persistent headache, and if developed in food by the action of an alkali on the plant, as in the use of soda for softening leguminous fruits, no one would dispute its tendency to produce nausea and vomiting.

In opposition to the preceding observations it is recorded that Tanret, in a communication made to the Society of Pharmacists of Paris, affirms to have found in the *Aethusa* neither an alkaloid nor a glucoside, nor any other substance to which a toxic action can be attributed. (Compare Planchon et Collin, "Les Drogues Simples," 1896, Tome II, p. 221, and Dorvault, "L'Officine," 1898, p. 376).

EXPERIMENTAL.

Our attention having been directed to the *Aethusa* as a plant which merited a more complete chemical examination than had hitherto been made of it, this was undertaken, and with a twofold object. In the first place it was evidently desirable that the constituents of the plant should be more precisely determined, and in the second place it was hoped that thereby it might be possible to arrive at a correct conclusion respecting its physiological action, which, as we have indicated, has long been a subject of dispute.

The importance of employing absolutely authentic material for this investigation was fully recognized, not only for the accurate determination of its constituents, but also in view of the possibility that the existing discrepancies of statement respecting the properties of the *Aethusa* are attributable to a confusion of plants of the same family which superficially resemble each other. That a confusion of this nature is possible, especially with umbelliferous plants, was shown by one of us several years ago,[1] when an investigation of a number of cases of poisoning, stated to have been caused by the so-called Wild Parsnip, revealed the fact that in every instance the virulent *Cicuta maculata* had been mistaken for the *Pastinaca sativa*, the latter, even in the uncultivated state, being perfectly innocuous.

The *Aethusa Cynapium* used in this investigation was collected during the months of July and August, at a time when the fruits were fully developed, but still green, as it was then presumed to be in a condition most favorable for the determination of its

[1] *Pharm. Rundschau*, New York, **9**, 162 (1891).

constituents and properties. It was gathered in districts both north and south of London, comprising a somewhat large area, for it was not very abundant in any particular locality. After its collection, each individual plant was carefully examined by a competent botanist, Mr. P. E. F. Perrédès, of London, and we had thus the assurance, not only of a proper identification, but also of the absolute freedom of the material from any contamination. The leaves of these plants, when bruised, had a faintly aromatic, herbaceous odor, and were entirely devoid of the disagreeable characters attributed to them in most botanical works. The green fruit, when bruised, differed only in having a somewhat stronger parsley-like odor.

A quantity of the entire fresh plants, amounting to 135½ pounds (about 61½ kg.), was dried in a warm atmosphere, and then weighed 26½ pounds (12 kg.), having lost about four-fifths of the original weight.

As a preliminary experiment, 25 grams of the ground dry herb were digested with Prollius' fluid, and evidence of the presence of a very small amount of alkaloid was thus obtained. Both the leaves and the fruit of the curled garden parsley, when tested in the same manner, afforded no reaction for an alkaloid.

In order to determine the constituents of the plant, 11 kg. of the air-dried material were completely extracted with hot alcohol. After the removal of the greater portion of the alcohol, the residual dark colored extract was brought into a flask, water added, and steam passed through the liquid until oily drops were no longer visible in the condenser. There then remained in the distillation flask a quantity of resinous substance (*A*) and a very dark colored aqueous liquid (*B*), both of which will be subsequently described.

Examination of the Steam Distillate.—The aqueous distillate was a milky liquid, containing some greenish oil on the surface. It was shaken out several times with ether, the ethereal liquid washed with water, dried with anhydrous sodium sulphate, and the ether removed. The residual oil was distilled under 20 mm. pressure, when it passed over between 80 and 175° C., leaving only a small quantity of dark, non-volatile substance. The distillate, amounting to 8.4 grams, was at first colorless, but soon became dark brown, and had a peculiar, rather unpleasant odor. On redistillation it was resolved chiefly into two fractions, one boiling between 80 and 100° C., and the other larger fraction

between 160 and 170° C., under 20 mm. pressure, but these were too small for further examination.

The aqueous liquid from which the volatile oil had been extracted contained a small amount of an acid, which was converted into a barium salt and found to consist chiefly of *formic acid*.

(*A*) *Examination of the Resins.*—The resinous substance contained in the steam distillation flask was removed from the aqueous liquid, washed with hot distilled water, and dried on a water-bath. It had a tarry consistency, a dark green color, and weighed 450 grams. In order to ascertain the character of this resin, 50 grams of it were mixed with prepared sawdust, the mixture dried and extracted successively in a Soxhlet apparatus, with the following solvents: Petroleum (b.p. 40°–50° C.) extracted 28.4 grams or 56.8 per cent.; ether, 7.1 grams or 14.2 per cent.; chloroform, 2.2 grams or 4.4 per cent.; ethyl acetate, 0.1 gram or 0.2 per cent.; alcohol, 3.3 grams or 6.6 per cent. Total, 82.2 per cent.

After extracting with these solvents the sawdust still retained a very dark color, and, as a considerable portion of the original substance had not been recovered, it was evident that this had undergone some change which had rendered it insoluble in alcohol.

The petroleum extract was a dark green, thick liquid, the other extracts were all resinous in character, and of a greenish or dark brown color.

The total remaining portion of resinous substance (400 grams) was then extracted successively in the above manner with light petroleum, ether, chloroform and alcohol.

(I) *Petroleum Extract of the Resins.*—About 250 grams of this extract were boiled for two hours with an alcoholic solution of 75 grams of potassium hydroxide. The alcohol was then removed, the dark greenish brown mass dissolved in water, in which it was only sparingly soluble, and the liquid shaken out with five successive portions of ether. The ethereal liquid was washed with water, dried with calcium chloride, and the ether removed. A quantity of dark orange-brown matter was thus obtained, which, when dissolved in alcohol and allowed to stand, deposited a crystalline substance. This substance, although repeatedly crystallized from alcohol and from ethyl acetate, persistently retained a yellow color. It melted at 72–74° C.,

and was not acted on by metallic sodium. In order to further purify it, it was distilled under 10 mm. pressure, when a colorless distillate was obtained, which was dissolved in ethyl acetate and allowed to crystallize It was then obtained in white glistening leaflets, melting sharply at 74° C., and was optically inactive.

0.0840 gram gave 0.2612 gram CO_2 and 0.1105 gram H_2O. C = 84.8; H = 14.6. $C_{35}H_{72}$ requires C = 85.4; H = 14.6 per cent.

This substance, therefore, appeared to be the hydrocarbon *pentatriacontane*, $C_{35}H_{72}$, the melting-point of which is given as 74° and 74.7° C.[1] So far as known to us, it is the first instance in which this hydrocarbon has been isolated from a plant.

The original alcoholic mother-liquors from the pentatriacontane were of a very dark brown color, and appeared to contain a large amount of resinous matter. After standing for some days, they deposited a small quantity of a substance in the form of crystalline plates, which was separated by filtration, and recrystallized four times from ethyl acetate containing some dilute alcohol. It was thus obtained in handsome pearly leaflets, which melted at 140–141° C. On analysis it gave the following results:

0.4000 gram, on drying at 110° C., lost 0.0213 gram H_2O = 5.3 per cent. $C_{26}H_{44}O,H_2O$ requires H_2O = 4.6 per cent.; $C_{24}H_{40}O,H_2O$ requires H_2O = 5.0 per cent.

0.1041 gram of anhydrous substance gave 0.3179 gram CO_2 and 0.1087 gram H_2O. C = 83.3; H = 11.6 per cent.; $C_{26}H_{44}O$ requires C = 83.9; H = 11.8 per cent.; $C_{24}H_{40}O$ requires C = 83.7; H = 11.6 per cent.

0.3787 gram of anhydrous substance, dissolved in 25 cc. of chloroform, gave α_D —1°.5′ in a 2 dcm. tube, whence $[\alpha]_D$ —35.7°.

When a small quantity of this substance was dissolved in chloroform, a little acetic anhydride added, and then a drop of concentrated sulphuric acid, a deep rose color was at once produced which rapidly changed to violet, then to an intense blue, and, after standing a short time, became green.

A portion of the substance was acetylated by boiling with acetic anhydride and anhydrous sodium acetate for about ten minutes. After the addition of water a product was obtained which, when crystallized from alcohol, formed colorless plates of a silky lustre, melting at 123–124° C

It is evident from these characters that the above-mentioned

[1] Compare Krafft: *Ber.*, **15**, 1715 (1882).

substance is either an isomeride of *phytosterol*, $C_{26}H_{44}O$, or a lower homologue.

The alkaline liquid, from which the pentatriacontane and phytosterol had been removed by means of ether, was concentrated, acidified with sulphuric acid, and distilled in steam. The distillate contained a small quantity of a greenish oil, which was removed by filtration and discarded. The acids contained in the filtrate were made into a barium salt, the concentrated solution of which gave the reactions of *formic acid*, and, when acidified with sulphuric acid, developed the odor of *butyric acid*.

The distillation flask contained a large quantity of a soft, dark green resin, which gave no indication of containing any fatty acids, and a brown aqueous liquid. The latter was decanted from the resin, and repeatedly extracted with ether, but it yielded nothing.

(II) *Ether Extract of the Resins.*—This extract was a dark green, nearly hard mass, which appeared to contain nothing crystalline. About 35 grams of it were fused with 200 grams of potassium hydroxide in the usual manner, the temperature of the melt being allowed to rise gradually to 260° C. After being allowed to cool, the mass was dissolved in water, acidified with sulphuric acid, and distilled in steam. The acids contained in the distillate were converted into a barium salt, and were thus identified as *formic* and *butyric acids*.

The liquid remaining in the distillation flask was decanted from a quantity of a friable, black resin, and repeatedly shaken out with ether. The ethereal liquid afforded a very small amount of a substance which gave the characteristic color reaction of *protocatechuic acid*.

(III) *Chloroform Extract of the Resins.*—This extract was relatively small in amount, and consisted of a friable, black resin, from which nothing crystalline could be obtained.

(IV) *Alcohol Extract of the Resins.*—This final extract, representing the portion of original resin which had remained undissolved by treatment with the preceding solvents, was dark brown in color, and appeared to contain nothing crystalline. On fusing 26 grams of it with 120 grams of potassium hydroxide, and treating the resulting product in the manner described in connection with the ether extract, it yielded the same substances as the latter, namely *formic* and *butyric acids*, together with a

substance which, after recrystallization, melted at 192° C. and gave the color reaction of *protocatechuic acid.*

(*B*) *Examination of the Aqueous Liquid.*—The aqueous liquid which was separated from the resinous matter after the distillation of the original alcoholic extract with steam, as previously described, was of a very dark brown color. It was concentrated to a thick syrup on the water-bath, then mixed with prepared sawdust, the mixture completely dried in a vacuum desiccator, and extracted in a Soxhlet apparatus with alcohol. This extract was concentrated and allowed to stand for some time, when a considerable quantity of a crystalline substance slowly separated, which was collected by filtration at the pump, washed with alcohol, and recrystallized from dilute alcohol. It was thus obtained in colorless needles, and was found to consist of an organic substance associated with potassium nitrate and chloride, from which it was impossible to free it by recrystallization. In order to isolate the organic compound, the possibility of its being an alcohol was considered, and the following method was therefore adopted. It was boiled for about five minutes with an excess of acetic anhydride and a little anhydrous sodium acetate, and the liquid, after being allowed to cool, shaken with a considerable quantity of water. A crystalline substance was thus precipitated, which was collected by filtration at the pump, washed with water, dissolved in hot alcohol, and allowed to crystallize. It then formed octahedral crystals, which melted at 122–123° C., and this melting-point was not changed by further crystallization; it was also recovered unchanged when again boiled with acetic anhydride for half an hour. When heated at 115° C. it did not lose in weight.

0.1025 gram gave 0.1875 gram CO_2 and 0.0568 gram H_2O. C = 49.9; H = 6.1. $C_{18}H_{26}O_{12}$ requires C = 49.8; H = 6.0 per cent.

0.4949 gram dissolved in 25 cc. of chloroform, gave $\alpha_D + 0°.52'$ in a 2 dcm. tube, whence $[\alpha]_D + 21.9°$.

The acetylated product thus agreed in composition with an hexaacetyl derivative of an hexahydric alcohol, which was evidently mannitol. For the purpose of comparison some hexaacetyl-*d*-mannitol was prepared from pure *d*-mannitol. After recrystallization from alcohol, it melted at 122–123° C., not at 119° C., as has been stated,[1] and a mixture of equal parts of this

[1] Beilstein's "Handbuch der organischen Chemie," Bd. I, p. 417.

preparation and the acetyl derivative of the crystalline substance obtained from the plant also melted at 122–123° C.

Further confirmation of the identity of our acetylated product was obtained by hydrolyzing it with 30 per cent. sulphuric acid, when it afforded a handsomely crystalline substance melting at 165–166° C. On analysis it gave the following result:

0.1114 gram gave 0.1616 gram CO_2 and 0.0768 gram H_2O. C = 39.5; H = 7.7. $C_6H_{14}O_6$ requires C = 39.6; H = 7.7 per cent.

The crystalline organic substance isolated from the *Aethusa* was thus definitely proved to be *d-mannitol*.

The sawdust with which the aqueous syrupy liquid had been mixed for the purpose of extraction with alcohol, as above described, was subsequently extracted with hot water, and to this aqueous extract was added the liquids from which the crystalline substance, consisting of mannitol and inorganic salts, had been obtained. The whole was then somewhat concentrated, and a solution of basic lead acetate added until no further precipitate was produced. A large quantity of a brownish yellow precipitate was thus obtained, which was separated from the aqueous liquid by filtration at the pump, and washed with a little water. A portion of this precipitate was suspended in water, decomposed by hydrogen sulphide, and the filtered liquid concentrated under diminished pressure. It afforded, however, only a dark brown syrup, containing uncrystallizable coloring-matter.

The filtrate from the basic lead acetate precipitate was freed from lead by means of hydrogen sulphide, again filtered, and the liquid concentrated under diminished pressure. A brown syrup was thus obtained from which nothing crystalline separated on standing. On warming a portion of this syrupy liquid with phenylhydrazine acetate, it readily afforded a crystalline glucosazone melting at 218° C., and evidently contained a large amount of *i-glucose*. The syrup, when warmed with potassium hydroxide, evolved ammonia, and it afforded precipitates with all the usual alkaloid reagents. Although these reactions might be attributed to substances of a proteid nature, the possibility of an alkaloid also being present was considered. The syrup was accordingly diluted with water, made alkaline with ammonia, and repeatedly shaken out with chloroform until nothing further was removed. The aqueous liquid, when acidified, was still precipitated by alkaloid reagents, but this behavior was doubtless due to proteid

matter. The chloroform solution was shaken out several times with dilute hydrochloric acid, the acid liquid then made alkaline with potassium hydroxide, and again shaken out with chloroform. This chloroformic liquid was washed with a little water, dried by means of potassium carbonate, and the chloroform removed. A small quantity of a thick, brown liquid was thus obtained, which possessed the characteristic, unpleasant odor of coniine. It was dissolved in dilute alcohol, and the solution, which had an alkaline reaction, exactly neutralized with hydrochloric acid. This liquid was then decolorized with animal charcoal, and evaporated in a vacuum desiccator, when a small brownish residue, containing needle-shaped crystals, was obtained. The solution of this substance gave precipitates with the usual alkaloid reagents, and with chlorauric and chloroplatinic acids.

As the characters of the substance above described suggested the presence of coniine or a closely related alkaloid, an attempt was made to obtain some further evidence of its identity. On account of the very small quantity of substance available, and the lack of specific reactions for the detection of small amounts of coniine, consideration was taken of the fact that this alkaloid on oxidation readily affords butyric acid.[1] The crystalline residue was therefore dissolved in water, and oxidized by heating with chromic acid on a water-bath. Steam was then passed through the liquid, and the acid contained in the distillate converted into the calcium salt. The solution of the latter, on evaporation, afforded a small amount of a salt which, when acidified with sulphuric acid, gave the odor of butyric acid, and, when warmed with absolute alcohol and sulphuric acid, developed the characteristic odor of ethyl butyrate.

In order to determine approximately the amount of volatile alkaloid contained in the fresh plant, about 40 kg. of the *Acthusa* were extracted with alcohol, and, after the removal of the greater portion of the solvent, caustic potash was added, and steam passed through the mixture. The distillate, which had an alkaline reaction, was acidified with hydrochloric acid, filtered to remove a small amount of essential oil, and the acid liquid concentrated under diminished pressure. It was then made alkaline with potassium hydroxide, shaken out repeatedly with chloroform,

[1] Compare Blyth: *J. Chem. Soc.*, **1**, 361 (1849).

the chloroformic liquid washed with water, dried with potassium carbonate, and the solvent removed. The residual oily liquid was dissolved in dilute alcohol, exactly neutralized with hydrochloric acid, the solution decolorized with animal charcoal, and evaporated to dryness in a vacuum desiccator. A residue containing needle-shaped crystals of the hydrochloride of the alkaloid was thus obtained, amounting to 0.12 gram, which is equivalent to 0.0003 per cent. of the weight of the entire fresh plant If the base be regarded as coniine, this would correspond to 0.093 gram or 0.00023 per cent. of the latter in the plant.

The small amount of alkaloidal salt obtained in the above-described operation was dissolved in a little water, and a solution of gold chloride added. An oily precipitate was thus produced, which did not become crystalline, even after standing for several days. It was finally dissolved in warm alcohol, and the solution filtered and concentrated, when a crystalline substance was obtained, but it was too small in amount to permit of further examination.

Physiological Tests.—In order to obtain further evidence respecting the character of the alkaloid found in the *Aethusa*, the following physiological tests were made:

(*a*) Five hundred grams of the ground, air-dry herb were extracted with acidulated water, the liquid made alkaline with caustic potash, and distilled in steam. The alkaline distillate was acidified with hydrochloric acid, concentrated under diminished pressure, again made alkaline with caustic potash, and shaken out with chloroform. The chloroformic solution was then extracted with very dilute acetic acid, and the whole of this liquid was administered *per os* to a small dog. Vomiting ensued within fifteen minutes, and was succeeded by profuse salivation which lasted for twenty-four hours. These effects were accompanied by an appearance of general weakness. After three days the animal had completely recovered.

(*b*) Five hundred grams of the ground, air-dry herb were completely extracted with hot alcohol, the solvent removed, and the resulting extract mixed with water. The aqueous liquid, separated from the soft resin by filtration, was concentrated under diminished pressure, and the whole of this preparation was administered to a small dog. Vomiting occurred within half an hour, and after this the animal seemed perfectly well.

(*c*) The whole of the resin separated from the preceding extract was administered to a dog but no effect of any kind could be observed.

It is evident from these results that the physiological action of the *Aethusa* is due to the volatile alkaloid, and the symptoms produced by the latter are those characteristic of coniine poisoning.

SUMMARY AND CONCLUSIONS.

In summarizing the results of this investigation the following essential facts may be noted.

The material employed consisted of the true *Aethusa Cynapium*, Linn., the identity of each plant having been carefully verified by a competent botanist, and it was perfectly free from any contamination. Both the fresh leaves and the green fruit of these plants, when bruised, were entirely devoid of the disagreeable odor attributed to them in most botanical works.

The more important constituents of the plant were found to be as follows:

(1) A small amount of an *essential oil*, of rather unpleasant odor. When first distilled it was colorless, but rapidly acquired a deep brown color. The amount of this oil obtained from an alcoholic extract corresponded to 0.015 per cent. of the weight of the entire fresh plant. The aqueous distillate from which the oil was separated contained a small amount of *formic acid*.

(2) An amount of *resinous substances* corresponding to 0.8 per cent. of the weight of the entire fresh plant. From the portion of this resin extracted by light petroleum there were isolated, after boiling with an alcoholic solution of potassium hydroxide, a small amount of a crystalline hydrocarbon, *pentatriacontane*, $C_{35}H_{72}$ (m. p. 74° C.), and a crystalline alcohol (m. p. 140–141° C.; $[\alpha]_D$—35.7°), which is either an isomeride of *phytosterol*, $C_{26}H_{44}O$, or a lower homologue. The alkaline liquid from which these crystalline substances had been extracted was acidified with sulphuric acid, which caused the separation of a quantity of soft resin, and the mixture, when subsequently distilled, yielded small amounts of *formic* and *butyric acids*. The portions of the original resin obtained by its subsequent extraction with ether and alcohol respectively, when fused with potassium hydroxide, yielded, in both cases, *formic*, *butyric*, and *protocatechuic acids*.

(3) A small amount of *d-mannitol* (m. p. 165–166° C.) from which a hexaacetyl derivative (m. p. 122–123° C.; $[a]_D + 21.9°$) was prepared. The mannitol, when first obtained, was associated with some potassium nitrate and chloride, and could only be separated from these inorganic substances by its conversion into the acetyl derivative.

(4) A considerable amount of inactive *glucose* and amorphous *coloring-matter.*

(5) An exceedingly small amount of a *volatile alkaloid*, having the peculiar, characteristic odor of coniine, and which, like the latter, yielded butyric acid on oxidation.[1] It was accompanied by a considerable amount of ammonia, which was probably produced for the most part by the decomposition of proteid substances contained in the plant. The amount of hydrochloride of the alkaloid obtained was 0.12 gram from 40 kg. of the entire fresh plant, which is equivalent to 0.0003 per cent. If the base be regarded as coniine, this would correspond to 0.00023 per cent. of the latter in the plant.

The isolation of a volatile alkaloid from the *Aethusa* may be regarded as of considerable interest, inasmuch as it was stated many years ago by Walz[2] that the fruit of this plant "contains a volatile base, very similar in odor and chemical behavior to coniine, and probably identical with it." A similar observation was recorded some years later by Bernhardt[3] while, on the other hand, Tanret[4] has subsequently stated that he could find in the *Aethusa* "neither an alkaloid nor a glucoside, nor any other substance to which a toxic action can be attributed."

It is, however, not only from a chemical point of view, but also from that of the toxicologist, that the verification of the presence of a volatile alkaloid in this plant merits consideration, particularly on account of the conflicting opinions which have so long prevailed respecting its reputed poisonous properties.[5] Although the amount of alkaloidal substance obtained from the plant was so small that its identity could not be definitely established by analytical data, a consideration of its physical and chemical characters, such as volatility, tendency to resinify, peculiar odor, and particularly the formation of butyric acid by its

[1] Compare *J. Chem. Soc.*, **1**, 361 (1849).
[2] *Neues Jahrbuch für Pharmacie*, **11**, 351–356 (1859).
[3] *Archiv. Pharm.* [3], **16**, 117 (1880).
[4] See Planchon et Collin, "Les Drogues Simples," 1896, Tome II, p. 221.
[5] Compare, especially, Dr. John Harley, *Pharm. Journ.*, **11**, 437 (1880).

oxidation, may reasonably lead to the assumption that it is either coniine or, possibly, a mixture of bases such as is obtained in a similar manner from *Conium maculatum*.

The fact that the proportion of alkaloid found by us in the *Aethusa* was so very small, and that the plant apparently contains no other substance to which a toxic action can be attributed, would seem to afford some justification for the conclusion of Dr. Harley[1] that it is free from the noxious properties which it has been stated to possess. It is quite possible, however, that this conclusion, based upon the results of physiological experiments with the expressed juice of the plant, may only be correct within certain limitations. It has been observed, for example, in the case of *Conium*, that the plant varies in narcotic power according to the stage of its development, and to the weather and climate, being most active when the fruit is still green, in hot and dry seasons, and in warm countries.[2]

Notwithstanding the contradictory nature of the statements that have been recorded respecting the properties of the *Aethusa*, and whatever may be the explanation of these discrepancies, there remains the important and positive fact that, in accordance with the observations of earlier investigators, the plant examined by us contained a small amount of a volatile alkaloid resembling coniine in its physical and chemical characters, and, as we have shown, also in its physiological action. In view of this fact, it can not be considered improbable that, under favorable conditions of growth, the proportion of alkaloid may be increased to such an extent as to impart to the plant the poisonous properties ascribed to it.

5-BROM-2-AMINOBENZOIC ACID AND SOME OF ITS DERIVATIVES.[3]

By Marston Taylor Bogert and William Flowers Hand.

Received October 17, 1905.

5-Bromacetanthranilic acid was prepared by the direct bromination of acetanthranilic acid, and also by the oxidation of 5-brom-*o*-acettoluide. Alt[4] proved that these two methods gave

[1] *Loc. cit.*

[2] Compare Farr and Wright: *Pharm. Journ.* [4], **18**, 185; "United States Dispensatory," Eighteenth Edition, p. 447, also Millspaugh: *Loc. cit.*

[3] Read at the Buffalo Meeting of the American Chemical Society, June 22, 1905.

[4] *Ber.*, **22**, 1643 (1889).

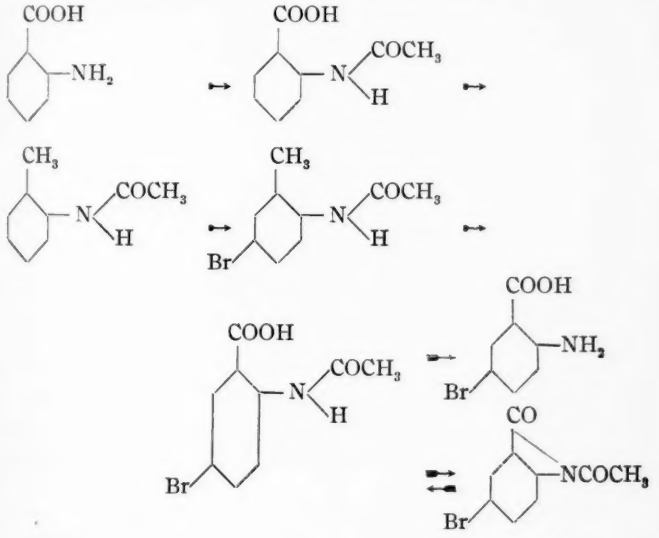
exactly the same product, and our own results confirm this fully. From the bromacetanthranilic acid, the bromanthranilic acid was obtained by saponifying with concentrated hydrochloric acid.

A great deal of time was spent in studying the barium salts of these two acids. The barium salt of the acetyl acid crystallizes in two forms, one approximately anhydrous, and the other carrying three and a half or four molecules of water, while that of the unacetylated acid crystallizes approximately anhydrous. In both cases, however, the analytical figures for barium were uniformly low. It seemed impossible to free these salts of all moisture below the point at which they decompose. Alt[1] mentions a barium salt of 5-bromanthranilic acid which crystallized with four molecules of water. This salt we did not encounter, possibly because our salt was prepared in a different way.

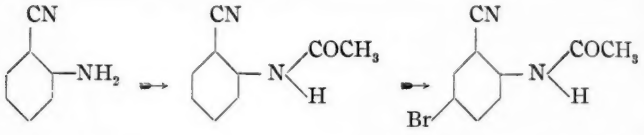
By treating the bromacetanthranilic acid with acetic anhydride, the corresponding bromacetanthranil was obtained.

We also prepared the bromacetanthranilic nitrile by direct bromination of acetanthranilic nitrile.

These various lines of work may be represented thus:



[1] *Loc. cit.*



Quinazolines were prepared from the bromanthranilic acid, its acetyl derivative, the bromacetanthranil, and from the bromacetanthranilic nitrile. These quinazolines will be described in a subsequent paper.

The authors wish to express their indebtedness to Messrs. H. J. Smith and J. E. Jacob, of the Chemical Laboratory of the Mississippi Agricultural and Mechanical College, by whom most of the analytical work required in this investigation was performed, and without whose willing and efficient coöperation the publication of this research would have been greatly delayed.

EXPERIMENTAL.

Acetanthranilic Acid.

Acetanthranilic acid, (1) $HOOC.C_6H_4.NHCOCH_3$ (2), was prepared according to the method of Jackson,[1] by the action of acetic anhydride upon anthranilic acid. A very good solvent for recrystallizing the crude product is 50 per cent. acetic acid. The pure acid is more or less difficultly soluble in cold water, toluene, carbon tetrachloride, chloroform, carbon disulphide, ether, cold aniline, cold dilute alcohol, or cold 50 per cent. acetic acid; moderately soluble in cold glacial acetic acid, cold 95 per cent. alcohol, or hot dilute alcohol; easily soluble in hot glacial or 50 per cent. acetic acid, hot 95 per cent. alcohol, hot aniline, or in acetone.

5-*Bromacetanthranilic Acid.*

5-Bromacetanthranilic acid, $C_6H_3(COOH)(NHCOCH_3)(Br)$ (1,2,5), was prepared (I) by the direct bromination of acetanthranilic acid, (II) by the oxidation of 5-brom-*o*-acettoluide, and (III) by the hydrolysis of 5-bromacetanthranil.

(I) *Preparation of 5-Bromacetanthranilic Acid by Brominating Acetanthranilic Acid.*—For satisfactory bromination the acetanthranilic acid must be in a very fine state of division; no lumps can be used.

The finely powdered acetanthranilic acid was placed in a round-bottomed flask, sufficient water added to form a thin paste, and a

[1] *Ber.*, **14**, 886 (1881).

solution of slightly more than the calculated amount of bromine dissolved in aqueous potassium bromide solution added gradually with shaking. The bromine was readily absorbed, and if the mixture was sufficiently dilute the temperature did not rise very rapidly. The addition of the bromine was continued until a yellow color was obtained that did not fade appreciably after standing for at least half an hour. The substitution was then complete. One hundred grams of acetanthranilic acid were thus brominated in the course of an hour. The product was very flocculent, and much more bulky than the original acetanthranilic acid. The thick mass was poured into a large porcelain dish, allowed to stand about twelve hours, filtered on a large Buchner funnel, and washed thoroughly. The precipitate was so fine that it clogged the filter and rendered the washing tedious and troublesome. The washed precipitate, when dry, was very light, and nearly colorless. It was dissolved in 95 per cent. alcohol, boiled with bone-black, filtered hot, hot water added to the filtrate to permanent cloud, and the solution allowed to cool. The crystals obtained, recrystallized from 50 per cent. acetic acid, separated in beautiful clear six-sided microscopic prisms, m. p. 218–219° (corr.). By recrystallization from glacial acetic acid, the melting-point was raised to 222–223° (corr.).

(II) *Preparation of 5-Bromacetanthranilic Acid by the Oxidation of 5-Brom-o-acettoluide.*—After experimenting with various methods of brominating *o*-acettoluide, we found that the use of the bromide-bromate mixture was the most satisfactory. The process used was as follows:

Fifty grams of *o*-acettoluide were dissolved in 500 cc. of 95 per cent. alcohol, the solution heated to boiling, a solution of 66.55 grams of potassium bromide in 200 cc. hot water added, the solution heated nearly to boiling, slightly more than sufficient hydrochloric acid added to decompose all potassium bromide, and a hot solution of 18.685 grams of potassium bromate dissolved in the least possible amount of water gradually stirred in. The brominated body separated suddenly. It was redissolved by continuing the heating and adding alcohol, if necessary, to prevent its enclosing unbrominated toluide. If the solution did not show excess of bromine at this point, a little more bromide and bromate were added until excess of bromine was evident. The bromtoluide was precipitated by the addition of a large amount of water, the

mixture cooled thoroughly, the precipitate filtered out, washed thoroughly and dried. It was purified by slow crystallization (on the steam-bath) from dilute alcohol, giving bundles of colorless, silky, microscopic hairs, m. p. 154° (corr.). Niementowski[1] gives the melting-point as 156–157°. As our product was entirely homogeneous and of fine appearance, we did not attempt to raise the melting-point by further recrystallizations, deeming it sufficiently pure for the preparation of the bromacetanthranilic acid. The yield of bromacettoluide was practically quantitative.

The dry bromacettoluide is very hard to wet again. We found it necessary to dissolve it in the least possible quantity of boiling acetone and reprecipitate with a large volume of boiling water. A mud-like mass resulted, which was readily oxidized by potassium permanganate.[2]

Fifty grams of the dry toluide were changed to this mud, and suspended in four liters of boiling water. The acetone was boiled out, and finely pulverized permanganate added gradually. The amount of permanganate required was between 300 and 400 grams. The mixture was kept boiling vigorously, and when once well under way the oxidation proceeded quite rapidly, and was complete in about two hours and a half. A test portion filtered off and cooled deposited no unchanged toluide, and the permanganate color was not discharged by further boiling. The excess of permanganate was then destroyed by adding alcohol, and the whole was filtered hot. The filtrate was allowed to stand about twelve hours, and in case any unoxidized toluide separated it was removed by filtration. The filtrate was acidified with hydrochloric acid (acetic acid does not transpose the salts of the acetamino acid, although it readily transposes those of the unacetylated acid), the precipitate washed well with water, treated with bone-black, and crystallized from toluene. Short, thick, small prisms were obtained, melting at 223–224° (corr.), identical with the bromacetanthranilic acid obtained by the direct bromination of acetanthranilic acid. The yield was good.

(III) *Preparation of 5-Bromacetanthranilic Acid by the Hydrolysis of 5-Bromacetanthranil.*—5-Bromacetanthranil was boiled with water, the precipitate filtered out, dried, and recrystallized from toluene. Small, clear, microscopic prisms resulted, m. p.

[1] *Ber.*, **25**, 868 (1892).

[2] Alt: *Loc. cit.*

221–222° (corr.), identical with the bromacetanthranilic acid prepared by the above two methods.

The pure 5-bromacetanthranilic acid forms crystals which appear under the microscope as beautiful, glassy, six-sided prisms. The melting-point of these crystals varies greatly according to the rapidity with which they are heated, as both Jackson[1] and Alt[1] observed. By rapid heating we have obtained as high a melting-point as 223–224° (corr.). The acid is difficultly soluble in water, carbon tetrachloride, chloroform, carbon disulphide, ligroin, 50 per cent. acetic acid, toluene, cold aniline, or cold dilute alcohol; moderately soluble in cold acetone, cold glacial acetic acid, cold 95 per cent. alcohol, or hot dilute alcohol; easily soluble in ether, hot aniline, hot glacial acetic acid, hot acetone, or hot 95 per cent. alcohol. It dissolves instantly and completely in solutions of the caustic alkalies or of ammonia. It decomposes alkaline carbonates or magnesium carbonate readily, but barium carbonate very slowly, the barium salt being very difficultly soluble. It is easily saponified by hot concentrated hydrochloric acid. Its salts are not transposed by acetic acid.

The acid was burned with the DeRoode mixture in a long combustion tube, and gave the following results: Found: C, 41.86; H, 3.26; Br, 31.03. Calculated for $C_9H_8O_3NBr$: C, 41.87; H, 3.10; Br, 31.00.

Barium Salt of 5-Bromacetanthranilic Acid.—The first experiments were conducted with bromacetanthranilic acid obtained by the bromination of acetanthranilic acid. These experiments were then repeated with bromacetanthranilic acid from bromacettoluide. The crystals obtained from the two series appeared identical under the microscope.

The bromacetanthranilic acid was boiled with excess of dilute barium hydroxide solution, the excess of barium precipitated by a stream of carbon dioxide, and the mixture filtered hot. On cooling, there first separated a mixture of transparent, microscopic, needle-like prisms, with a few larger, six-sided, transparent prisms. By filtering off the first crop of crystals, other crops separated from the mother-liquor containing less and less of the microscopic needles and more and more of the larger prisms. The larger prisms were finally obtained apparently free from the needles, but we were not able to secure any first crop crystals

[1] *Loc. cit.*

consisting exclusively of the microscopic needles. The two crystalline forms are easily distinguishable under the microscope. A great many analyses were carried out on the various crops of barium salt, but the results were not very satisfactory. We are of the opinion, as the result of these analyses, that the microscopic needles which separate first are anhydrous, while the larger prisms carry three and a half or four molecules of water. It is difficult to remove all the water from the hydrated crystals below the temperature at which the salt itself is decomposed. The barium salt is very difficultly soluble in water even at its boiling-point.

5-Bromanthranilic Acid.

This was prepared by saponifying 5-bromacetanthranilic acid with boiling concentrated hydrochloric acid. The bromacetanthranilic acid used was prepared both from acetanthranilic acid and from the bromacettoluide. Both products gave one and the same bromanthranilic acid, as Alt[1] showed some time ago.

One hundred grams of 5-bromacetanthranilic acid were placed in a two liter round-bottomed flask, and boiled for three hours under a return condenser with 800 cc. of concentrated hydrochloric acid. The hydrochloride of the amino acid is difficultly soluble in concentrated hydrochloric acid. During the boiling a stream of dry hydrogen chloride is passed through the solution. This diminishes the bumping which generally occurs, and keeps the solution saturated with hydrochloric acid gas, so that on cooling with ice practically all of the hydrochloride of the amino acid is precipitated. This precipitate is filtered out, washed with cold, concentrated hydrochloric acid, sucked dry on the pump, and transferred to a large porcelain dish. It is then covered with fifteen volumes of cold water, cracked ice is added, and most of the hydrochloric acid is neutralized with ammonia. It is not advisable to attempt to neutralize the hydrochloric acid completely, as the hydrochloride is completely dissociated by the large volume of water added. The free amino acid is filtered out, washed thoroughly with ice water, recrystallized and treated with boneblack. Toluene proved a very satisfactory menstruum for crystallization of the substance.

5-Bromanthranilic acid forms colorless crystals. When rapidly heated, they melt at 219–220° (corr.), with previous softening. Alt[1] gives the melting-point as 211.5–212°. The acid is insoluble

[1] *Loc. cit.*

or difficultly soluble in water, benzene, toluene, xylene, ligroin, oil of turpentine, carbon tetrachloride, carbon disulphide, ethyl acetate, cold chloroform, or cold dilute alcohol; moderately soluble in hot chloroform, in dry ether, or cold acetone; easily soluble in hot acetone, in hot dilute alcohol, in 95 per cent. alcohol, or in aniline. The copper salt is apple-green, as Alt[1] states, and not bright blue as reported by Hübner and Petermann.[2]

Some of the acid was purified through its barium salt. In decomposing the solution of the barium salt with hydrochloric acid, the solution should be cold and the acid added gradually, or the amino acid may precipitate in a gummy condition difficult to filter and wash. An excess of hydrochloric acid does no harm, as the hydrochloride is immediately dissociated by the excess of water.

Analysis of the purified acid gave the following results: Found: C, 38.32; H, 2.72; Br, 37.55. Calculated for $C_7H_6O_2NBr$: C, 38.89; H, 2.73; Br, 37.02.

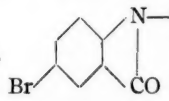
Hydrochloride of 5-Bromanthranilic Acid.—Dry hydrogen chloride was passed through a warm solution of the acid in absolute ether. The precipitated hydrochloride was filtered out and dried. It is rapidly decomposed by moisture. A small amount, washed a few times with cold water on a filter, and the residue then dissolved in nitric acid, gave no reaction at all for chlorine ions. The salt gives off hydrochloric acid quite rapidly even in the air.

Barium Salt of 5-Bromanthranilic Acid.—The purified acid was suspended in boiling water, dilute barium hydroxide solution added to slightly alkaline reaction and the boiling continued for some time, adding more baryta water, if necessary. The excess of barium was precipitated by carbon dioxide, the solution filtered boiling hot, and allowed to cool slowly. Transparent, six-sided prisms separated in mossy colonies. These crystals were anhydrous. They darken slightly on standing, are very difficultly soluble in cold water, and only moderately soluble in boiling water.

Alt,[1] by boiling the acid with barium carbonate, obtained a salt carrying four molecules of water. This salt we did not encounter.

[1] *Loc. cit.*

[2] *Ann. Chem.* (Liebig), **149**, 133.

5-Bromacetanthranil, 

—5-Bromacetanthranilic acid was boiled with an excess of acetic anhydride. The crystals which separated on cooling were filtered out, dried, and recrystallized from carbon tetrachloride.

The pure anthranil crystallizes in colorless scales, m. p. 131° (corr.).

The following figures were obtained on analysis: Found: C, 45.04; H, 2.50; N, 6.24 and 6.16; Br, 33.31. Calculated for $C_9H_6O_2NBr$: C, 45.01; H, 2.13; N, 5.83; Br, 33.32.

5-Bromacetanthranilic Nitrile.

5-Bromacetanthranilic Nitrile, $C_6H_3(CN)(NHCOCH_3)(Br)(1,2,5)$. —Acetanthranilic nitrile (m. p. 132.5° (corr.)) was brominated by suspending it in water and passing in a current of air laden with bromine vapor. Five or six hours were required to complete the bromination. The crude product was filtered out, washed, treated with bone-black, and recrystallized from water. Larger crystals were obtained from carbon tetrachloride. During the bromination the temperature of the liquid must not be permitted to rise above about 30°, or the product may be spoiled.

The pure nitrile forms clear, six-sided prisms, m. p. 158° (corr.); insoluble or difficultly soluble in cold water, carbon disulphide, cold benzene, or cold carbon tetrachloride; moderately soluble in cold dilute alcohol, hot water, cold toluene or hot carbon tetrachloride; easily soluble in 95 per cent. alcohol, hot dilute alcohol, acetone, ethyl acetate, hot benzene, hot toluene, or chloroform.

Bromine found, 33.52; calculated for $C_9H_7ON_2Br$, 33.46.

COLUMBIA UNIVERSITY AND
MISSISSIPPI AGRICULTURAL AND MECHANICAL COLLEGE,
October, 1905.

ON THE OCCURRENCE OF ARSENIC IN WINES.

BY H. D. GIBBS AND C. C. JAMES.

Received September 25, 1905.

WHILE engaged upon the analysis of 100 samples of California dry, red wines, the frequent occurrence of coal-tar dyes induced us to test for arsenic which is often found in certain dyes. We

were surprised to find that arsenic occurred in many samples which were otherwise free from unnatural ingredients. This led to a rather extended investigation of the subject, and in all 329 samples have been examined by various methods for the presence of arsenic compounds. The quantities found were in all cases small, and while in all probability the compounds of the element are not to be met in quantities sufficient to produce toxic effects, we have undertaken this investigation in the attempt to throw some light upon the source of this constituent, as it is undoubtedly an accidental ingredient. It is not beyond the realms of possibility that the source, if not discovered, might give rise to increasing quantities until the limit of tolerance would be reached. This in fact occurred in English beers some years ago when the brewers used glucose prepared with a sulphuric acid which contained considerable quantities of arsenic.

It is recognized that arsenic administered with alcohol[1] may be more toxic than when administered alone, owing to the more rapid assimilation caused by the stimulation of the gastric mucosa. Moreover, the system with continued use, becomes tolerant of large amounts of arsenic, and some individuals, owing to inherent idiosyncrasies, are much more resistant than others to its toxic effects. By employing special methods Gautier[2] has shown that arsenic is a remarkably uniform constituent of animal and vegetable organisms and a widely distributed element, but as we have not employed in this investigation his methods[3] for the estimation of minute quantities we do not consider that all of the arsenic which has been found is an unavoidable constituent of the wines examined.

Opposition to the use of artificial coloring substances in French

[1] C. H. Tattersall (Report on Arsenical Poisoning, Borough of Salford, Eng.; H. Tappeiner: *Z., Biol.*, **16**, 497 (1881), and "Physiological Chemistry," by A. Gamgee, 438 (1893)), as a result of experiments upon dogs and cats in which he had ligatured the pylorus before injecting into the stomach solutions of various alimentary and poisonous substances, came to the conclusion that the stomach absorbs only very small quantities of bodies which are introduced into it in aqueous solution, while, on the other hand, it appears readily to absorb dilute alcohol and substances dissolved in alcohol. When sulphate of strychnia was injected into the stomach of cats with ligatured pylorus, death from strychnia poisoning ensued in a period varying between one and one-half and three hours, while with unligatured pylorus death occurred from the same dose in eight minutes. If, however, strychnia were dissolved in dilute alcohol and injected into the stomach of a cat, with ligatured pylorus, death occurred in ten minutes.

[2] *Bull. Soc. Chim.* [3], **27**, 843 (1902); [3], **29**, 31 (1903); A. Gautier and P. Clausmann, *C. R.*, **139**, 101 (1904); V. Bordas: *Ibid.*, **139**, 234 (1904).

[3] *Bull. Soc. Chim.*, [3], **29**, 859; *Ann. Chim. Phys.* [5], **8**, 384; Bertrand: *Bull. Soc. Chim.* [3], **27**, 847 (1902).

wines in 1876 led to the discovery that arsenic might thus be introduced into the wine, and Gautier[1] says that arsenic should always be looked for in wines containing aniline colors. In the same year C. Husson[2] published an article on "The Detection and Estimation of Fuchsine and Arsenic in Wines Which Have Been Colored with Fuchsine." J. Clouet[3] found that caramel, which is frequently used in conjunction with fuchsine, often contains large amounts of arsenic.

The outbreak of arsenical poisoning[4] at Manchester, England, in 1900 was traced to beer in which arsenic was introduced through the glucose. This epidemic led to an extensive consideration of rapid methods for the determination of arsenic, beginning with the Reinsch test and ending with the adoption of the electrolytic method of Thorpe[5] by the Royal Commission on Arsenical Poisoning. We have tried a large number of methods and various combinations and modifications and found none as satisfactory as the Marsh, using zinc and sulphuric acid.

Our investigations began with the analysis of 100 samples of dry red wines.[6] The ash obtained from the quantitative determination of the total solids and ash, by the method of the Association of Official Agricultural chemists,[7] using 50 cc. of wine, was dissolved in dilute sulphuric acid (1 to 3), filtered and introduced into the Marsh generator. By this rather rough method 15 of the 100 samples produced perceptible mirrors which were identified as arsenic by conversion into arsenious oxide tetrahedra. Twelve of these samples seemed to be pure wines, three contained in addition to the arsenic, coal-tar dyes, and one contained benzoic acid. Fourteen of these samples were bottled wines and one was taken from the cask. These results led to a systematic study of methods in order to assure ourselves that the arsenic was not introduced through the reagents or apparatus used, and that all the arsenic present in the wine was obtained in the mirror. The only methods employed were those by which the arsenic was finally obtained in the form of a mirror deposited upon the inner surface of a glass tube by the breaking down of arsine by heat.

[1] *Bull. Soc. Chim.*, **25**, 483, 530 (1876).
[2] *C. R.*, **83**, 199. Report on Arsenical Poisoning, Borough of Salford, 1900, p. 47.
[3] *Annales d'Hygiène Publique*, 1878, p. 145.
[4] Report of Medical Officer of Health at Manchester, December, 1900.
[5] *J. Chem. Soc.*, **83**, 974 (1903); *J. Soc. Chem. Ind.*, p. 965 (1903).
[6] Bulletin San Francisco Board of Health, March, 1905.
[7] U. S. Dept. Agr., Bureau of Chem., Bull. **65**, 83.

The methods used for the conversion of the arsenic compounds into arsine include the electrolytic method of Thorpe[1] and the Marsh method, using zinc and hydrochloric acid and zinc and dilute sulphuric acid. After carefully testing the reagents for the Marsh method, hydrochloric acid was discarded in favor of sulphuric acid, and Kahlbaum's special granulated zinc was found on the whole to be most satisfactory. Twenty grams of this zinc were placed in the Marsh generator and completely dissolved in sulphuric acid (1 to 3), which required two and one-half hours. These reagents gave no signs of a mirror. The sulphuric acid employed was that manufactured by Baker and Adamson and, later in the investigation, acid manufactured by the Mallinckrodt Chemical Works was used with equal success. This test was repeated with zinc from each different lot employed and with several samples from each lot, with the same result. The action of the acid on the zinc was started with a few drops of a dilute solution of chlorplatinic acid.[2] Copper sulphate[3] and iron alloyed with the zinc have been used for this purpose, but it has been shown[3] that a part of the arsenic is retained in the generator by these reagents.

A Florence flask of about 250 cc. capacity was used as a container for the zinc and sulphuric acid. This was fitted with a two-holed rubber stopper, through one hole of which passed a separatory funnel for introduction of the sulphuric acid and the arsenic solution, the outlet tube passing through the other hole. As rubber will absorb arsine, care was exercised to have the exposed surface of the rubber as small as possible. The same rubber stopper and connections and apparatus were used throughout the investigation, with the exception of the Florence flask, which had to be renewed once. The outlet tube was connected with a 4-inch U-tube arranged so that the issuing gases first passed through a spiral of lead acetate paper and then through granulated calcium chloride, held in place by plugs of absorbent cotton. From the U-tube the gases passed into a Jena glass tube of 0.7 cm. internal and 1.0 cm. external diameter drawn down to a constriction from 10 to 15 cm. long[4] and 2 mm. external diameter.[5] These tubes were cleaned by standing in a mixture of nitric and

[1] *Loc. cit.*
[2] Gautier: *Ann. Chim. Phys.* [5], **8**, 384 (1876).
[3] Parsons and Stewart: This Journal, **24**, 1005 (1902).
[4] G. Bertrand: *Loc. cit.*
[5] W. Thompson: *Chem. News*, **86**, 179 (1902).

chromic acids, after which they were washed with water, alcohol and ether, and dried by aspirating a current of air through them. To decompose the arsine, this Jena glass tube, protected by wire gauze, was heated by two or three Bunsen burners for a space of 10 to 15 cm. before the constriction. The solution containing the arsenic was slowly added to the contents of the generator through the separatory funnel, after the air was completely expelled from the apparatus by allowing the action of the sulphuric acid on the zinc to proceed until the apparatus was full of hydrogen, or by running a rapid current of carbon dioxide through the apparatus before the sulphuric acid was introduced. The latter method seemed preferable as it avoids using up the zinc and the consequent concentration of the solution with salts, which, of necessity, retards the action of the acid on the zinc. If any oxygen is allowed to remain in the apparatus, the mirror will deposit white, probably due to the formation of the arsenious oxide. By this method when the amount of arsenic in the mirror was less than 0.1 mg. the formation of the mirror was practically complete in one hour and often in less time. However, the uniform time of one hour was adopted for each determination. After each determination the apparatus was thoroughly cleaned and a fresh quantity of zinc added.

Another generator used with less success was the electrolytic type described by Thorpe.[1] This method, although it is the official one in England, we discarded for the reason that samples of wine which we found by the Marsh method to contain arsenic failed to show even traces by the electrolytic method. Another disadvantage is that the arsenic must be in the arsenious condition before introduction into the generator.

The preparation of the solution for introduction into the generator offers some difficulty, and many methods were tried. Since the wine is acid in character, it might be supposed that there would be a loss of arsenic by evaporating the sample direct on the water-bath and then ashing the residue, as was done in the case of the first 100 samples. On evaporation, however, the wine loses its acid character and the ash is decidedly alkaline. To avoid the volatilization of the arsenic, several methods for destroying the organic matter were tried.[2] It was found impra-

[1] *Loc. cit.*

[2] Report of Royal Comm. on Arsenical Poisoning, *J. Soc. Chem. Ind.*, **23**, 159 (1904).

ticable to make the wine alkaline with sodium carbonate before evaporation, for the residue, on ashing, chars and fuses before a white ash can be obtained. The Chittenden[1] method was used for some time, but was finally discarded for the method finally adopted, as the mirrors obtained were not as heavy, and moreover it required more time and careful attention. The method finally adopted and used in the analysis of 229 samples of wine was that which had been used by Newlands and Ling[2] in determining arsenic in coal. In the case of the wines, 50 cc. are made alkaline with milk of lime, evaporated to dryness on the sand-bath and ignited at a low red heat. The method is very rapid and the condition of the ash is all that could be desired. There is no fusion or swelling and the method is particularly adapted to wines with a high per cent. of sugar. The ash is taken up with dilute sulphuric acid (1 to 3) filtered and the filtrate introduced into the generator.

Quantitative determinations were made by comparison with a set of standard mirrors ranging from 0.01 mg. to 0.1 mg. of metallic arsenic. These were made by adding the required amount of a standard solution of arsenious oxide to 50 cc. of arsenic-free wine and allowing this to run in the generator for one hour. Other mirrors were made by adding the arsenious oxide solution directly to the generator. The tubes were sealed off while the apparatus was still running, thus preserving the mirror in an atmosphere of hydrogen to insure permanency.[3] Little difference was discernible in the standards prepared by these different methods. However, a careful inspection of the mirrors reveals the fact that the 0.02 mg. standards are more than twice as heavy as those made by the introduction of 0.01 mg. of arsenic. The increase is more regular and uniform in the standards above 0.02 mg. We are led to believe that a small amount of arsenic is always retained in the generator. This amount seems to be uniform and uninfluenced by the amount of arsenic present in the solution tested. Perhaps it is retained by the platinum or by small amounts of iron which may be present in the zinc.

Two hundred and fifteen dry red wines, thirteen dry white wines and one sweet wine were tested by this method. Fifty cc. of the sample were employed in most cases but in a number of

[1] *Am. Chem. J.*, **2**, 235.
[2] Newlands: *J. Soc. Chem. Ind.*, 1901, p. 736; 1904, p. 166.
[3] *Loc. cit.*

instances 300 cc. were used. We consider it a mere coincidence that the white wines and the sweet wine examined gave no mirrors, and it is to be regretted that the press of other work prohibited the examination of more samples. Of the dry, red wines nineteen showed less than 0.01 mg. of arsenic per liter and four gave mirrors showing the presence of larger amounts. Eighteen of these samples were taken from casks and five were bottled wines. We have no knowledge of the date of the bottling. Twenty samples contained arsenic, and no other unnatural substance was found to be present. Five contained arsenic and a coal-tar dye and one contained benzoic acid. The four samples highest in arsenic calculated as the metal are:

(1) 0.05 mg. per liter or one part in 20,000,000.

(2) 0.025 mg. per liter or one part in 40,000,000. Benzoic acid also found.

(3) 0.05 mg. per liter or one part in 20,000,000. Coal-tar dye also found.

(4) 0.013 mg. per liter or one part in 80,000,000.

The largest amount of arsenic found in wines by Gautier and Clausmann[1] is 0.009 mg. per liter, or about 1 part in 111,000,000.

In the examination of some 200 samples, representing about 30,000,000 gallons of wine, C. S. Ash,[2] has found some samples which contain larger amounts.

There are a number of sources to which it might be possible to attribute the introduction of the compounds of arsenic. Some of these, which appear to us to be the most probable, we have investigated in detail.

(1) The cultivation of vines on arsenical soils. It is an established fact that certain amounts of arsenic compounds are tolerated by plants. Stoklasa[3] concludes from experiments with oats that while arsenic can not replace phosphoric acid in the living cell it may increase the development of the organs of assimilation in the plant. Pot experiments[4] to investigate the absorption of arsenic by barley showed that most of the arsenic occurred in the grain. Arsenic was applied at the rate of eleven pounds per acre, but the soil itself was found to contain a greater

[1] *Loc. cit.*

[2] Mr. Ash, chemist of the California Wine Association, has informed us that the amounts found in the three samples highest in arsenic are, 1 part in 6,000,000, 1 part in 8,000,000, and 1 part in 14,000,000.

[3] *Ann. Agron.*, **23**, 471; Abst. *Expt. Sta. Record*, **9**, 1028.

[4] *Expt. Sta. Record*, **14**, 346.

amount. No data concerning grapes are at hand but it is possible that there may be a tendency for the arsenic to accumulate in the fruit. Gautier[1] has found that arsenic occurs in the largest proportions in the external covering of animals, the hair, skin and nails, and it is possible that the skin of the grape may contain larger amounts than the other portions of the plant. If this is true, the fact that larger amounts of arsenic were found in the red than in the white wines[2] would be in part accounted for, as the red wines are fermented with the skins while the white are not.

(2) The spraying of vines with arsenical insecticides, a practice which we are informed is rarely if ever practiced in California, would be a very probable source, especially in regions where there is little or no rainfall to wash away the arsenic compounds during the season in which the grapes are gathered.[3] A. M. Peter[4] reports that appreciable quantities of both copper and arsenic were found in tobacco which had been sprayed with Paris green. The practice of spreading upon the ground arsenical mixtures[5] for the purpose of poisoning grasshoppers and other insects is quite general in some localities.

(3) The use of sulphuric acid in cleaning vats used in the

[1] *Loc. cit.*

[2] Mr. Ash has also observed that the red wines show the larger amounts of arsenic.

[3] *Ann. Rep. State Vit. Comm.* (Calif.), 1887, 82. "Most of the enemies of the vine feed directly upon the foliage—the grasshopper, rabbits, squirrels, army worms, or sphynx-moth worm, beetles, scribe, false chinch bug, cut worms, etc. * * * Theold—yes, the oldest remedy—Paris green or London purple, known to be destructive generally, has been brought into requisition. Extensive experiments have this year been conducted * * * to prove that a 'solution' of Paris green or London purple—one pound to one hundred and sixty gallons of water—may be used to spray the foliage of the vine, while the grapes are small, with perfect safety to the consumer of the grapes, wine, or raisins produced therefrom. The efficacy of the remedy as a destroyer, is not questioned; but to determine whether, in California where the summer rains do not fall, a condition dissimilar to that found in sections where the remedy is known—I say whether here, it could be used with the same guarantee of safety or not, seemed to me a question important enough to merit a trial. It is my pleasure to announce a perfect success; the products, grapes and wine, were carefully examined by Professor Rising, state analyst, and proved innocuous."

[4] *Ky. Sta. Rep.*, 1893, p. 14.

[5] W. B. Rising: *Loc. cit.* "As a final test, I myself picked in spots where the arsenic had been used most freely, from thirty to forty pounds of grapes in each of the different vineyards. These were examined for arsenic. In none did I obtain more than the faintest trace of this substance, an amount absolutely inappreciable, and too small to have any perceptible action upon the human body." "In this examination of the grapes they were carefully and repeatedly washed with dilute solution of caustic potash, and finally with pure water. The wash-water and alkali were evaporated to a small volume, and then tested by Marsh's apparatus for the presence of arsenic." "A few words of caution should be added to what I have said in regard to the use of this deadly poison. It is a poison, and this must always be kept in mind. It (referring to arsenic, mixed with bran, middlings and syrup, made into a stiff paste and then set upon the ground for the purpose of killing grasshoppers) should be gathered up and not left upon the land."

process of fermentation and casks used for storing and shipping. Sulphuric acid in its crude form invariably contains arsenic, and its use in cleaning vats, tanks, barrels and other wooden vessels may easily introduce small quantities of arsenic.

(4) The use of any substance in the manufacture of which sulphuric acid has been employed. This will include some coal-tar dyes, some preservatives and glucose. Glucose has in the past been a very notable source of arsenic and arsenical poisoning. No data are at hand concerning the extent of its use in the wine industry. Moreover, since the experience of the brewers in England, the glucose manufacturers are very careful to avoid arsenical compounds in their process. Our experience would lead us to believe that little or no arsenic is introduced by the use of coal-tar dyes and the common preservatives, except sulphur dioxide, for many of the wines which were found to be artificially colored and preserved failed to show any traces of arsenic.

(5) The use of sulphur in sulphuring casks and wines. T. L. Phipson[1] says that some samples of Naples sulphur contain a notable amount of arsenic and that some Silician sulphur is quite exempt. Japanese and French sulphurs are found in large quantities upon this market, the former in predominating amounts. The samples obtained were analyzed in two different ways: first by oxidation with fuming nitric acid, heating with sulphuric acid to remove the nitric acid and introducing the resulting solution into the Marsh apparatus; second by oxidation in a current of oxygen. For this purpose a hard glass tube was drawn down to a small size and bent to a right angle at the beginning of the constriction, so that it could be introduced into an absorption bottle, the point dipping below the water which was used to absorb the gases. The sulphur was introduced into the tube in a porcelain boat and heated gently in the current of oxygen until the combustion started, after which no heating was required. After the combustion was complete the boat and tube were washed with a dilute solution of sodium hydroxide which was added to the contents of the absorbing bottle. Aliquot parts of this solution were made acid and introduced into the Marsh apparatus after the sulphur dioxide was removed either by boiling or by oxidation with iodine solution. The reagents used were tested by a sufficient number of blank determinations. The two methods gave results which agreed in a satisfactory manner.

[1] *Chem. News*, **83**, 61 (1901).

Results.—Flowers of sulphur, Japanese. One gram, oxidized by means of fuming nitric acid, gave a mirror of 0.2 mg. One part arsenic in 5,000 of sulphur.

Japanese Sulphur.—1.9162 grams burned in a current of oxygen, the resulting solution made up to 300 cc., and 50 cc. portions introduced into the Marsh apparatus, gave 0.045 mg. mirrors. One part arsenic in about 7,000 parts of sulphur. One gram, oxidized with fuming nitric acid, the whole of the resulting solution being introduced into the Marsh apparatus, gave a mirror so heavy that it could not be accurately estimated quantitatively by comparison with our set of standards. A fairly close agreement, however, was apparent.

French Sulphur.—1.5586 grams burned in oxygen, the resulting solution made up to 250 cc. and 50 cc. portions introduced into the Marsh apparatus, gave mirrors of 0.01 mg. One part arsenic in about 30,000 parts of sulphur.

Three other samples analyzed showed smaller amounts of arsenic, one sample in particular showing merely traces.

These sulphurs are made into candles and burned in casks before wine is introduced in order to thoroughly disinfect the casks, one-half to one candle (containing about 30 grams of sulphur) being used to a cask of 62 gallons. After the sulphur is burned the cask is sometimes rinsed. In sulphuring the wines, in order to stop the fermentation, the sulphur candles are burned over the wine which is contained in a vessel only partially filled. Much of the sulphur dioxide escapes and is not absorbed by the wine but it is possible that all or nearly all of the arsenic present in the sulphur, the arsenious oxide being less volatile, will pass into the wine. It is difficult to estimate the amount of arsenic which may be introduced into the wine by this process. On the basis of four sulphur candles containing 30 grams of sulphur each and arsenic in the largest proportion (which we found namely one part in 5,000) being used for 500 gallons of wine, there would be thus introduced into the wine arsenic in the proportion of about 0.01 mg. per liter. There is no doubt that these figures are not excessive for some wines and in the case of white wines the amount of arsenic thus introduced may be double or treble this amount. Some of the arsenic which we have found present in the wine can thus be accounted for; however, red wines are

rarely, if ever, sulphured and one would naturally suppose that more arsenic would be introduced in the process of sulphuring the wine than in sulphuring the cask and other receptacles.

(6) The use of clarifying agents (such as isinglass, gelatine and compounds of casein with soda) which contained arsenic was found[1] to introduce some arsenic into beer, and it is possible that some of the arsenic in wines may be traced to the same source. We have made no tests upon any of these substances.

(7) Yeast which has come in contact with arsenical solutions will take up arsenic and carry contamination to solutions in which it may afterwards be placed.[2]

(8) The glass of bottles in which wine is aged and shipped might be a source of some of the arsenic. Large quantities of arsenious oxide are used in the glass industry,[3] and this fact has suggested the possibility of the introduction of some arsenic into wine which has acted upon glass on long standing in the bottles.[4] Two bottles of the style in common use, one clear glass and one very dark, were tested for arsenic by several methods. The bottles were broken into small pieces, sampled, crushed quite fine, again sampled and ground in an agate mortar to an impalpable powder. One-gram samples were fused in platinum crucibles with fusing mixtures composed of sodium carbonate and potassium nitrate, sodium carbonate and potassium carbonate, the fused mass dissolved in sulphuric acid (1:3) and introduced into the Marsh apparatus. No traces of arsenic could be obtained from the dark glass, and only the very slightest traces from the clear glass. Repeated analyses gave the same result. Even though the entire amount of arsenic was not obtained in the mirror by this method it is evident that, as a source of arsenic in the bottled wines, the glass is not very promising.

(9) Lead shot used in cleaning bottles may account for the introduction of small quantities of arsenic. The practice of using

[1] *Loc. cit.*

[2] Report beer, brewing and other materials, 1900 and 1901, Manchester, Eng., by S Delepine.

[3] W. Fresenius: *J. Soc. Chem. Ind.*, 1884, p. 263.

[4] Hovestadt: *Jena Glass. Trans.*, 1902, p. 412. "It is true that the substance put into the mixture (glass) is As_2O_3, but in all Jena glass oxidizing materials (nitrates) are added. These convert the lower oxide into the higher during melting, and in the glass as finally obtained the As_2O_5 is combined with alkali. Dr. Schott adds that, in many commercial glasses, such as plate and sheet glasses, As_2O_3 is employed without the addition of oxidizing materials, so that no As_2O_5 can be formed, but he adds that, in his opinion, no arsenic then remains in the glass—it is driven off in vapour and exercises no influence."

second-hand bottles is quite prevalent in the wine industry. These bottles are almost invariably cleaned by the use of lead shot. The peculiar shape of the common wine bottle with its hollow bottom, forms an ideal receptacle for the lodgement of shot, the dark glass completely masking their presence. The lead,[1] which invariably contains arsenic, will in time go into solution in the wine and thus introduce some arsenic. The largest arsenic mirrors which we have obtained were from the first lot of 100 samples almost all of which were bottled wines.[2] Some of these samples had undoubtedly been in the bottles for a number of years; one in particular, which gave an excellent mirror, bore an internal revenue stamp of the series of 1898. It is to be regretted that quantitative measurements of these mirrors were not made, the reason being that a set of standards was not then completed, and the mirrors were destroyed on further tests to prove the presence of arsenic. However, it is impossible to account in this way for more than a part of the arsenic found, for nineteen of the samples which were found to contain arsenic were taken directly from wooden vessels and remained in bottles especially cleaned under our direction, only a short time pending analysis.

(10) The metal pipes and pumps used in conveying the wines, and the filters may be the source of some very small quantities.

SUMMARY AND CONCLUSIONS.

(1) We find that arsenic, in small quantities, occurs as an accidental ingredient of some wines, and we have undertaken this investigation for the purpose of locating the source for the benefit of the wine industry. We are confident that as soon as the origin is discovered this ingredient will practically disappear as a menace.

(2) Total number of samples examined, 329; number in which arsenic was found, 38.

Of the samples containing arsenic, nineteen were bottled wines and nineteen were taken from the cask.

(3) The largest amounts found and measured quantitatively

[1] Lead was not found in any of the wines. However, if present at any time in the wine, it may have been thrown out of the alcoholic solution as lead sulphate.

[2] It has been stated to us, in explanation of the occurrence of the largest amounts of arsenic in the older wines, that the use of arsenical sprays was much more common a few years ago than at present.

are one part in 20,000,000.[1] The limit of tolerance set by the British Commission on Arsenical Poisoning for beer is 0.01 grain per gallon, about one part in 7,000,000. This limit as applied to wine would undoubtedly be considered too exacting, for wine is usually consumed in much less quantities than beer.

(4) In all probability arsenic does not occur in quantities sufficient to ever produce toxic effects; however, much of that found can undoubtedly be excluded by care upon the part of those engaged in the wine industry.

(5) The arsenic which is present in some samples of wine can not in our opinion be attributed to one source.

(6) The most probable sources of the major part of that found are, arsenical sprays when used upon the vines, sulphur burned for the purpose of sulphuring the wines and receptacles, and perhaps to some extent the lead shot used in cleaning the bottles.

[1] Subsequent analyses have revealed the presence of larger amounts of arsenic than any previous investigations of wines. Nine samples of dry, white California wines, selected from a winery which furnished us with a sample of sulphur containing arsenic in the proportion of 1 part in 5,000, gave the following results:

		Mgs. SO_2 per liter.	Arsenic, 1 part in
1.	Hock	126	25,000,000
2.	Sauterne	120	25,000,000
3.	White wine blend	7	trace
4.	Johannisberger	206	10,000,000
5.	Riesling	42	trace
6.	Sauterne	181	trace
7.	Riesling	79	15,000,000
8.	Hock	51	5,000,000
9.	White wine blend	77	10,000,000

It is not certain that all of these wines were treated with the same kind of sulphur. Fourteen samples of wines found upon the eastern markets and of eastern manufacture, gave varying amounts of arsenic, one sample in particular containing the largest amount yet discovered.

1.	Sherry	Contained salicylic acid.	trace
2.	Ives seedling		no mirror
3.	Catawba		trace
4.	Delaware		20,000,000
5.	Virginia seedling	Contained coal-tar dye and salicylic acid.	20,000,000
6.	Sweet catawba		15,000,000
7.	Catawba		10,000,000
8.	Port		10,000,000
9.	Catawba	Contained salicylic acid.	8,000,000
10.	Ives seedling		40,000,000
11.	Claret		2,500,000
12.	Delaware	Contained salicylic acid.	20,000,000
13.	Claret		trace
14.	Port		trace

FOOD LABORATORY OF THE BOARD OF HEALTH,
SAN FRANCISCO, CALIF.
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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 116.]

THE DETECTION, DETERMINATION, AND RATE OF DISAPPEARANCE OF FORMALDEHYDE IN MILK.

BY R. H. WILLIAMS AND H. C. SHERMAN.

Received October 25, 1905.

IT IS well-known that when very small amounts of formaldehyde are added to milk, the latter is not permanently preserved and the color reactions indicating the presence of formaldehyde gradually become less distinct, and may finally fail. The suggestion has frequently been made that milk may be preserved for market with such a small proportion of formaldehyde that the latter will have disappeared before a sample can be tested by the analyst, who will thus fail to detect the adulteration. So far as we are aware, however, no direct evidence of such cases has been advanced. Apparently, but little attempt has been made to study the disappearance of the formaldehyde by quantitative methods. Smith[1] states that if milk containing formaldehyde is kept cool, it may stand one or two days, at least, without alteration in the amount obtained on analysis, even when the original amount was only 1:50,000. He adds that a trial proved that when milk containing formaldehyde is subjected to a warm and varying temperature, the amount of formaldehyde recovered by distillation is only 55 to 60 per cent. of that recovered from the same sample when fresh. On the other hand, Rivas[2] reports that even when kept in a refrigerator, mixtures of formaldehyde and milk 1:10,000 or 1:20,000 showed a marked decrease of the formaldehyde after two days, while if only 1:50,000 was added, the disappearance of the preservative was more rapid, being so nearly complete at the end of two days that only a weak or doubtful reaction was obtained. At higher temperatures the formaldehyde disappeared somewhat more rapidly.

Rivas' results thus indicate a much more rapid disappearance of formaldehyde than was found by Smith. In view of this discrepancy and of the fact that preservatives are added to milk mainly for the sake of saving the cost of refrigeration, we have

[1] This Journal, **25**, 1037 (1903).

[2] *Univ. of Penn. Medical Bulletin*, **17**, 175 (1904).

studied the detection and determination of formaldehyde with special reference to the rate at which it disappears from milk kept at ordinary room temperatures.

QUALITATIVE DETECTION.

The hydrochloric acid and ferric chloride test, as developed by Leach, has been found very satisfactory in this laboratory. Ten cc. of the milk to be tested are mixed, in a porcelain casserole, with an equal volume of concentrated hydrochloric acid containing about 2 mg. of ferric chloride, and the mixture heated slowly, rotating the casserole occasionally to insure solution of the curd, and finally kept at a temperature just below boiling for about a minute, unless a distinct reaction is previously obtained. In the presence of formaldehyde a violet color develops, otherwise the solution slowly turns brown. Regarding the delicacy of this test Leach states:[1] "By this test 1 part of formaldehyde in 250,000 parts of milk is readily detected before the milk sours. After souring, the limit of delicacy proves to be about 1 part in 50,000."

In an experiment to test the question whether the sourness of the milk in itself affected the delicacy of the test, we obtained two samples from the same source, one fresh and sweet showing a total acidity equivalent to 0.18 per cent. lactic acid, the other four days old, sour, curdled, and showing an acidity equivalent to 0.92 per cent. lactic acid. To each of these samples formaldehyde was added in the proportion of 1 : 100,000. On applying the test as given above, perfectly distinct reactions were obtained in both cases, the test being apparently just as delicate in one case as in the other. We therefore interpret Mr. Leach as claiming, not that the test is less delicate for the detection of formaldehyde in sour milk, but that (1) the delicacy of the test is about 1 : 250,000; (2) when 1 part of formaldehyde is added to 50,000 parts of milk and the mixture allowed to stand until the milk has become sour, enough of the preservative will still be present to be shown by this test. We have confirmed each of these claims. Sometimes, however, the browning of the heated mixture renders indistinct the violet color produced by such minute quantities of formaldehyde. In these cases, more satisfactory indications are obtained on carrying out the test with the fol-

[1] "Food Inspection and Analysis," p. 140.

lowing slight modification.[1] After heating the milk with the acid reagent as described, keeping the temperature just below the boiling-point for about a minute, add quickly from 50 to 75 cc. of cold water and observe the color carefully at the moment of dilution. The purplish violet color, which becomes apparent upon dilution, fades very rapidly, so that the advantage of this modification is entirely lost unless great care is taken to note the appearance immediately upon adding the water.

The gallic acid test, while less convenient, is, in our experience, fully as characteristic as the hydrochloric acid and ferric chloride test, and considerably more delicate. The sample of milk to be tested is acidulated with sulphuric acid and distilled in the same way as for the quantitative determination of the formaldehyde. To 5 cc. of the distillate, add 0.2 to 0.3 cc. of a saturated solution of gallic acid in alcohol and float the mixture upon pure concentrated sulphuric acid in a test-tube. In the presence of formaldehyde a blue color develops gradually at the plane of contact. The reaction is shown distinctly by pure solutions containing 1 : 500,000 of formaldehyde, and there is no reason to doubt that it is equally delicate when applied to the detection of formaldehyde in milk. A sample of milk which originally contained 1 : 50,000 formaldehyde ceased to give any reaction by the hydrochloric acid and ferric chloride test after five days, but the distillate subsequently obtained from 30 cc. of this sample gave an unmistakable formaldehyde reaction when tested with gallic acid.

QUANTITATIVE DETERMINATION.

For the determination of formaldehyde, 300 cc. of milk in a round-bottomed flask of about 1 liter capacity are acidulated with 3 cc. of dilute (1 : 3) sulphuric acid and distilled over a small rose-top burner until 60 cc. of distillate are obtained. The formaldehyde in this distillate is determined by the potassium cyanide method.[2] About one-third of the formaldehyde[3] in the milk is recovered in this way.

The following results were obtained upon freshly prepared solutions:

[1] Sherman : *School of Mines Quarterly*, **26**, 408 (1905) ; "Methods of Organic Analysis," p. 228.

[2] Romijn : *Z. anal. Chem.*, **36**, 18 (1897) ; Smith : This Journal, **25**, 1028 (1903); Williams : *Ibid.*, **27**, 598 (1905).

[3] Leonard and Smith : *Analyst*, **22**, 5 (1897).

FORMALDEHYDE IN WATER.

1 : 1000 distilled at once ; 36.1 per cent. recovered.
1 : 5000 " " " 36.6 " " "
1 : 10,000 " " " 34.0 " " "
1 : 40,000 " after 2 days ; 38.9 " " "

FORMALDEHYDE IN MILK.

1 : 10,000 distilled at once ; 31.9 per cent. recovered.
1 : 20,000 " " " 34.3 " " "

These results agree so closely with those obtained by Smith[1] that further tests of the method upon fresh solutions seemed unnecessary.

RATE OF DISAPPEARANCE.

Quantitative determinations show a gradual disappearance of formaldehyde even from its solutions in distilled water, the rate of disappearance being more rapid the more dilute the solution. For example:

Solution in distilled water 1 : 1000 after 168 days[2] showed 99.6 per cent. of the formaldehyde originally present.

Solution in distilled water 1 : 5000 after 168 days showed 56.8 per cent. of the formaldehyde originally present.

Solution in distilled water 1 : 10,000 after 168 days showed only traces of the formaldehyde.

These determinations were made by the potassium cyanide method which has been shown[3] to include as formaldehyde any paraformaldehyde which may be present. Hence the low figures obtained upon the more dilute solutions show an actual destruction, and not merely a polymerization of formaldehyde. In the experiments upon the disappearance of formaldehyde in milk, parallel determinations upon water solutions of the same concentration have been made by the distillation method described above, distilling until the distillate measures one-fifth the volume of sample taken.

The principal results obtained in studying the rate of disappearance of the formaldehyde are given in the following tables, the first of which shows the figures obtained by the approximately quantitative method outlined above, while the second shows the intensity of the color reactions obtained by the hydro-

[1] This Journal, **25**, 1036 (1903).

[2] The bottles containing these solutions had been opened several times.

[3] Wi liams : This Journal, **27**, 598 (1905).

chloric acid and ferric chloride test, at different intervals after adding the formaldehyde to the milk. The account of experiments by Bigelow[1] indicating a somewhat more rapid disappearance of this reaction was received during the writing of this paper.

DISAPPEARANCE OF FORMALDEHYDE AS SHOWN BY APPROXIMATELY QUANTITATIVE ESTIMATIONS.

Series No.	Description of sample.		Distilled after standing.	Proportion of original formaldehyde recovered in distillate (one-fifth volume). Per cent.	formaldehyde estimated to have disappeared. Per cent.
1.	Formaldehyde added to :				
	Milk	1 : 10,000	2 days	25	38
	"	1 : 20,000	2 "	23	42
	"	1 : 40,000	2 "	10	75
	Water	1 : 40,000	2 "	39	—
	Milk	1 : 10,000	4 "	20.5	48
	"	1 : 20,000	4 "	3.7	90
	"	1 : 40,000	4 "	Trace	(Nearly all)
	Water	1 : 40,000	4 "	36	8
	"	1 : 40,000	9 "	25	38
	"	1 : 40,000	18 "	16	60
	"	1 : 40,000	28 "	10	75
2.	Formaldehyde added to :				
	Milk	1 : 10,000	17–25 days	5–6	85
	Water	1 : 10,000	11 "	37	5
3.	Formaldehyde added to :				
	Fresh milk	1 : 1000	117 "	21	43
	Sour milk	1 : 1000	133 "	20	45
	Water	1 : 1000	149 "	39	—
	Fresh milk	1 : 5000	117 "	3.9	90
	Sour milk	1 : 5000	135 "	3.1	92
	Water	1 : 5000	156 "	22	42
4.	Formaldehyde added to :				
	Diluted milk[2]	1 : 20,000	1 day	[3]	25
	Water	1 : 20,000	11 days	[3]	25
	Diluted milk[2]	1 : 40,000	1 day	[3]	25
	Water	1 : 40,000	11 days	[3]	45

[1] Bull. 90, Bur. Chem., U. S. Dept. Agriculture.

[2] Milk diluted with an equal volume of distilled water.

[3] Figures not comparable with those given in this column on account of differences in experimental methods.

DISAPPEARANCE OF FORMALDEHYDE IN MILK AS INDICATED BY COLOR REACTION WITH HYDROCHLORIC ACID AND FERRIC CHLORIDE.

Formaldehyde added in proportion of	Tested after standing.	Reaction obtained.	Condition of sample.
1 : 250,000	½ hour	Fair	Fresh
1 : 250,000	2 days	None	Very sour, completely curdled
1 : 100,000	½ hour	Strong	Fresh
1 : 100,000	2 days	Faint	Sour and curdled
1 : 100,000	5 "	?	Curd separated
1 : 50,000	2 "	Fair	Sour and curdled
1 : 50,000	5 "	?	Curd largely separated
1 : 40,000	4 "	Fair	Sour
1 : 40,000	14 "	Faint	Curdled and separated
1 : 20,000	4 "	Strong	Curdled, very sour, some gas
1 : 20,000	46 "	Faint	Curd dissolving
1 : 20,000	66 "	"	" "
1 : 20,000	216 "	None	Curd mostly dissolved
1 : 15,000	150 "	"	" " "
1 : 10,000	46 "	Distinct	Sour and curdled
1 : 10,000	66 "	"	" " "
1 : 10,000	216 "	Faint	Curd largely dissolved
1 : 5000	216 "	Strong	Curdled
1 : 1000 (A)	350 "	"	Normal
1 : 1000 (B)	15 months	"	Slight evidence of digestion
1 : 1000[1] (C)	3 years	Distinct	Curd largely digested
1 : 1000[1] (D)	3 "	None	" " "
1 : 1000[1] (E)	4 "	"	" " "
1 : 800[1]	3 "	Distinct	" " "
1 : 600[1]	5 "	Strong	Loose precipitate of curd, no apparent digestion

SUMMARY OF PRINCIPAL RESULTS.

By the method here used an approximate estimation of formaldehyde in milk can be made at any concentration greater than 1 : 160,000 and the rate of disappearance can be studied quantitatively until this dilution is reached.

Aqueous solutions containing 1 : 5000 to 1 : 40,000 of formaldehyde lost strength steadily on standing at room temperature, the loss increasing with the dilution and being due to an actual destruction and not merely to polymerization of the formaldehyde.

Formaldehyde added to milk in such proportions as are most likely to be used commercially (1 : 10,000 to 1 : 40,000), disappeared ten to twenty times as rapidly as from water solutions

[1] In these cases the amount of formaldehyde added is only approximately known.

of the same concentration. Thus formaldehyde added to distilled water in the proportion of 1:40,000 had diminished to 1:160,000 in twenty-eight days, while in a parallel experiment with milk it showed the same diminution in two days.

Stronger solutions are much more stable. Formaldehyde in water 1:1000 showed no appreciable loss in five months. The rate of disappearance of formaldehyde from milk containing 1:1,000 was practically the same as from water containing 1:5,000.

The rate of disappearance did not seem to be affected by allowing the milk to become sour before adding the formaldehyde.

The hydrochloric acid and ferric chloride test for formaldehyde in milk is sensitive to a dilution of 1:250,000. Sourness of the milk does not in itself diminish the delicacy of the reaction, but when milk is preserved by means of formaldehyde the latter will have largely disappeared before the milk becomes sour. In all of the cases here studied, however, distinct reactions were obtained at least as long as the milk remained sweet and of normal appearance. That these results indicate a less rapid disappearance of formaldehyde than was found by Rivas or by Bigelow is thought to be due mainly to the greater delicacy of the test as modified for our experiments, though doubtless differences in laboratory temperature and in the nature of the milk used may also have affected the results.

The gallic acid test is much more delicate than the hydrochloric acid and ferric chloride test and gives more conclusive results with samples which have stood until the formaldehyde has largely disappeared.

QUANTITATIVE LABORATORY, COLUMBIA UNIVERSITY,
NEW YORK, October, 1905.

THE PHOSPHATES OF CALCIUM. I.[1]

BY F. K. CAMERON AND A. SEIDELL.

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WHEN the phosphates of calcium are brought into contact with water they are partially decomposed, owing to hydrolysis. At ordinary temperatures this decomposition generally proceeds at a very slow rate, and in consequence equilibrium conditions

[1] Published by permission of the Secretary of Agriculture.

have probably been attained in but very few of the experiments which have been described hitherto.

The purpose of this investigation was to determine the composition of the resulting solutions and the solids in contact with them in the system water (H_2O), lime (CaO), and phosphoric acid (P_2O_5), under conditions of final equilibrium at a definite temperature and throughout a wide range of concentration. The temperature selected was 25°, and the concentration of phosphoric acid (P_2O_5) varied up to nearly 540 grams per liter of solution, the concentration with respect to lime varying in consequence to a maximum of 77 grams per liter.

Several series of solutions were prepared by adding so-called tricalcium phosphate, dicalcium phosphate or monocalcium phosphate to solutions of phosphoric acid. After prolonged standing or heating, the containing bottles were rotated for some time in a water-bath kept at a constant temperature. When the contents of the bottles were to be analyzed, they were allowed to stand until the solid material had settled. A weighed amount of the solution was made up to definite volume and aliquot portions were taken for analysis. By subtracting the sum of the weights of the lime and phosphoric acid contained in a given volume of solution from the total weight of the solution, the weight of the water present was determined.

In the analyses the lime was determined by taking an aliquot, adding a large excess of ammonium oxalate and heating to incipient boiling. Ammonia water in excess was then added and the solution kept for some time on the hot plate at a temperature just below boiling. If the solution remained turbid, more ammonium oxalate was added until it was certain that this salt was present in excess, and a granular precipitate settled to the bottom of the vessel, leaving a clear supernatant solution. When it appeared necessary, the filtered and washed calcium oxalate was redissolved and again precipitated in the usual way. In this way a satisfactory separation of the phosphoric acid from the lime was effected and the latter was then determined in the usual manner, weighing as oxide. The phosphoric acid was determined by the volumetric method of the Association of Official Agricultural Chemists.[1]

[1] Bull. No. 46, Division of Chemistry, U. S. Dept. Agriculture (1899), p. 11.

As equilibrium is reached at quite a slow rate, several series of mixtures were made by different methods.

Series A.—To solutions of phosphoric acid of concentrations up to about 200 grams per liter, Kahlbaum's tricalcium phosphate was added until a solid residue was left which did not dissolve even after long standing.

Series B.—To solutions of phosphoric acid of the above concentration dicalcium phosphate was added until a solid residue was left.

Series C.—Monocalcium phosphate containing an excess of phosphoric acid was added to water until a solid persisted. The results of this last series have already been published.[1] Owing to a typographical error in misplacing a decimal point the results for calcium, as printed, are one-tenth the correct value. Making the correction, it is possible to calculate approximately, from the data given, the ratio of phosphoric acid to calcium in the solid residue, although exact ratios cannot be calculated since the specific gravities of the solutions were not determined.

The identification of the solid phases in contact with the solutions was an essential feature of the investigation. For this purpose microscopic examinations were made in some instances, but the chemical analyses were made in all cases. The solids could not be separated from the adhering solution, and so portions of the solids, together with the adhering liquid, were removed, weighed and analyzed for the amounts of lime and phosphoric acid present. The water was then known by difference. The composition of the solid phases in contact with the solutions was determined by an algebraic formulation.

Suppose P to represent the total phosphoric acid found in the solid residue and adhering solution, P_1 the phosphoric acid actually in the solid, P_2 the phosphoric acid dissolved in the adhering solution, and L, L_1, L_2 the corresponding values for lime. Then

$$P = P_1 + P_2 \qquad (1)$$

and

$$L = L_1 + L_2. \qquad (2)$$

Suppose W represent the total water found in the solid and adhering solution, W_1 the water combined in the solid, and W_2 the water in the adhering solution. Then

$$W = W_1 + W_2. \qquad (3)$$

[1] This Journal, **26**, 1454 (1904).

If the ratio between the water and the phosphoric acid in the solid W_1/P_1 be taken as m and the ratio to lime W_1/L_1 be taken as n (m and n being constants readily calculated from the formula of the substance) then substituting in (3), it follows that

$$W_2 = W - m\ P_1 \tag{4}$$

or

$$W_2 = W - n\ L_1. \tag{5}$$

Then

$$\frac{P_2}{W_2} = \frac{P_3}{W_3} \tag{6}$$

and

$$\frac{L_2}{W_2} = \frac{L_3}{W_3}, \tag{7}$$

where P_3, L_3 and W_3 represent the phosphoric acid, lime and water respectively in any given volume of the supernatant solutions, whose compositions have been determined. Substituting (1) and (4) in (6), it follows that

$$\frac{P - P_1}{W - mP_1} = \frac{P_3}{W_3}$$

whence

$$P_1 = \frac{PW_3 - P_3W}{W_3 - mP_3}, \tag{8}$$

and similarly

$$L_1 = \frac{LW_3 - L_3W}{W_3 - nL_3}. \tag{9}$$

The absolute values of P_1 and L_1 are of little interest, but their ratio will determine the nature of the solid in the residue, hence

$$\frac{P_1}{L_1} = \frac{(PW_3 - P_3W)\ (W_3 - nL_3)}{(W_3 - mP_3)\ (LW_3 - L_3W)}.$$

For monocalcium phosphate [$CaH_4(PO_4)_2.H_2O$], $n = 0.9643$, $m = 0.3800$ and $P_1/L_1 = 2.5$; for dicalcium phosphate ($CaHPO_4.2H_2O$), $n = 0.8035$, $m = 0.6338$ and $P_1/L_1 = 1.3$; for tricalcium phosphate [$Ca_3(PO_4)_2$], n and m disappear and $P_1/L_1 = 0.85$. These ratios are sufficiently wide apart in magnitude to make the identification of the corresponding phosphates an easy matter, and consequently in applying the above formula to the experi-

mental data only four-place logarithms were used and in the tabulated results the ratios are given only to the first decimal place.

It will be seen from the table that the analyses of the solid phases in contact with the solutions yielded a constant ratio (P_2O_5: CaO) of about 1.3, which is the ratio for dicalcium phosphate, $CaHPO_4.2H_2O$. That equilibrium conditions had been realized was assured, for in Series *A* the solid initially added to the acid solutions was tricalcium phosphate, and finally the solid was dicalcium phosphate; and in Series *C* the solid initially used was monocalcium phosphate, and finally the solid was dicalcium phosphate; while in Series *B*, dicalcium phosphate was dissolved in phosphoric acid solution and the solid in excess again proved to be dicalcium phosphate. Thus starting from solids in which the ratio of P_2O_5 to CaO is greater than, equal to, or less than 1.3, the ratio finally obtained in all cases was 1.3, showing that a solid containing P_2O_5 to CaO in this ratio is the stable phase in each case, and it is safe to conclude that dicalcium phosphate is the solid phase over the range of concentration in the three series. It should be further pointed out that the points on the diagram, in which the abscissas are CaO per liter and ordinates P_2O_5 per liter, all lie on a smooth curve, another indication that equilibrium had been reached.

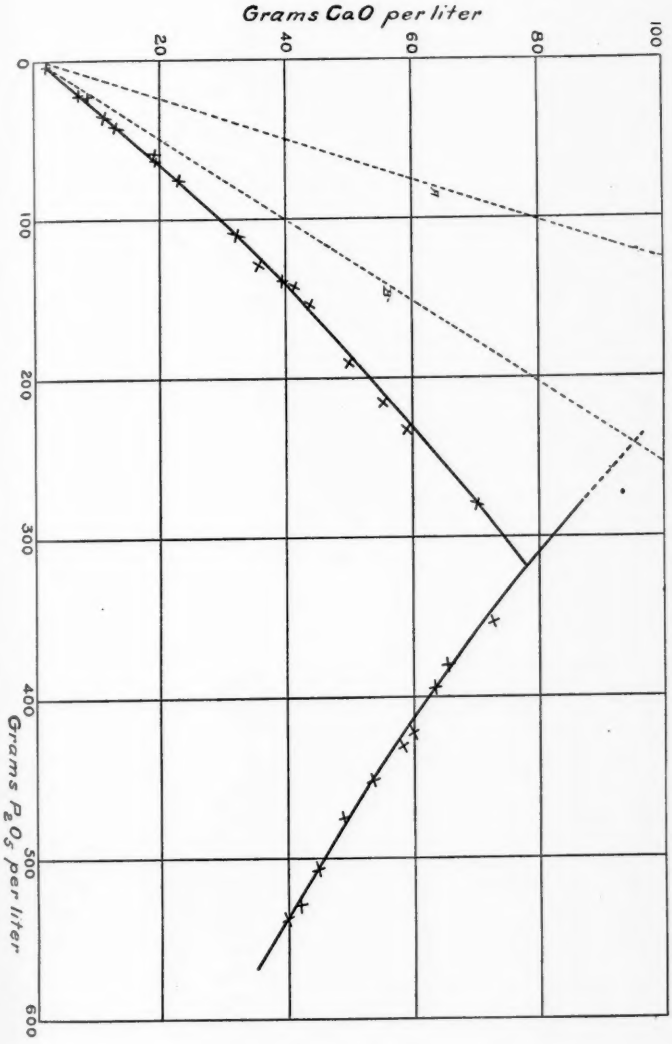
Two further series of solutions were prepared, using more concentrated solutions of phosphoric acid than those employed in the first three series. In one case, Series *D*, the solid added initially was monocalcium phosphate, while in the other case, Series *E*, the solid added was dicalcium phosphate. The analyses of the solid phase show that in every case it was undoubtedly monocalcium phosphate [$CaH_4(PO_4)_2.H_2O$], the ratio of P_2O_5 to CaO varying but little from the calculated ratio 2.5. That equilibrium had been reached was indicated by the fact that the points obtained from two differently prepared series all lay on a smooth curve; also in Series *D* monocalcium phosphate goes into solution as such and the solid phase remaining has the same composition as the solid originally added, while in Series *E* there is a complete change in the composition of the solid from dicalcium phosphate to monocalcium phosphate.

The results obtained from the several series are given in the following table, and the concentrations of the solutions are represented in the accompanying chart.

COMPOSITION OF AQUEOUS SOLUTIONS OF LIME AND PHOSPHORIC ACID.

Series.	CaO per liter solution. Grams.	P_2O_5 per liter solution. Grams.	Ratio P_2O_5/CaO in solid.
A	1.71	4.69	1.2
C	7.48	22.39	1.4
A	8.10	23.37	1.3
A	11.57	36.14	1.3
C	12.88	41.24	1.5
A	18.77	59.35	1.3
C	19.25	63.03	1.4
A	23.31	75.95	1.2
C	23.69	79.10	1.5
A	32.41	109.8	1.3
A	35.90	129.8	1.3
A	39.81	139.6	1.3
A	40.89	142.7	1.3
A	43.82	154.6	1.3
B	49.76	191.0	1.4
B	55.52	216.5	1.3
B	59.40	234.6	1.4
B	70.31	279.7	1.5
E	72.30	351.9	2.4
E	69.33	361.1	2.4
E	65.46	380.3	2.4
E	63.53	395.1	2.4
E	59.98	419.7	2.6
E	59.25	424.6	2.4
D	57.74	428.0	2.6
D	53.59	451.7	2.2
D	48.78	475.3	2.2
D	44.52	505.8	2.3
D	41.86	528.9	2.4
D	39.89	538.3	2.5

When the results for concentrations in solution are plotted (see Fig.) it will be seen that they fall upon two curves. The curve representing the series of solutions in contact with dicalcium phosphate as solid phase, shows an increasing concentration of lime with increasing concentration of phosphoric acid, while on the contrary the curve representing the series of solutions in contact with monocalcium phosphate as solid phase, shows a decreasing concentration of lime with increasing concentration of phosphoric acid. Both curves approximate straight lines, although there is evident a slight curvature in the one representing the solutions in contact with dicalcium phosphate. The intersection of the two curves at which point both mono- and dical-


Grams CaO per liter
0
20
40
60
80
100
100
200
300
400
500
600
Grams P_2O_5 per liter
II
III

cium phosphate are stable solid phases in contact with the solution, is found by interpolation to represent a concentration of approximately 77 grams lime and 317 grams phosphoric acid per liter of solution, the solution having a specific gravity of approximately 1.29 as compared with pure water at the same temperature.

It has been noted by many investigators that when monocalcium phosphate is added in large amount to water, agitation, long standing, or rise of temperature will cause a precipitate of dicalcium phosphate to form. This fact suggests the possibility of monocalcium phosphate existing in meta-stable equilibrium in contact with a solution containing less phosphoric acid than that required by the triple point as charted. Experiments showed that such meta-stable conditions could be obtained rather readily, but no attempt was made to see how far the monocalcium curve could be extended.

The two dotted lines on the diagram indicate the systems in which the ratio P_2O_5:CaO is the same as in the compounds $CaHPO_4$ and $CaH_4(PO_4)_2$, respectively. The line *A* does not cut the curve representing the solution in equilibrium with solid dicalcium phosphate and hence it is impossible at the temperature 25° to obtain a solution in equilibrium with a solid of the composition $CaHPO_4.2H_2O$. On the other hand, the line *B* cuts the curve representing the solutions in equilibrium with monocalcium phosphate, but the point of intersection is in a field unstable with respect to dicalcium phosphate. It is therefore possible, theoretically, to obtain a solution of monocalcium phosphate in equilibrium with monocalcium phosphate of the composition $CaH_4(PO_4)_2.H_2O$.

Tricalcium phosphate, when brought into contact with water, always gives a solution with an acid reaction,[1] this fact having been observed many years ago by Warington.[2] Repeated washing of the solid residue finally leaves a product which yields a solution neutral to litmus, but containing a smaller ratio of P_2O_5

[1] Apatite, of which a number of specimens from different sources have been examined, always gives a solution with an alkaline reaction. But many specimens of South Carolina and Tennessee rock phosphate give solutions with acid reaction to litmus, as does also the precipitated product of the laboratory. It is further worthy of note that when these phosphates which give an acid solution are powdered or precipitated in a finely divided form and are shaken up with a solution of litmus, on settling they carry down all the coloring-matter with them, leaving the supernatant solution clear and colorless, though still quite acid, as can be seen by adding more litmus to the decanted liquor.

[2] *J. Chem. Soc.*, **26**, 983 (1873).

to CaO than that required by the formula $Ca_3(PO_4)_2$. It is possible to precipitate products containing still smaller ratios of P_2O_5 to CaO which yield solutions containing more lime than phosphoric acid and which are alkaline to such indicators as litmus or phenolphthalein. Some preliminary attempts were made to follow the solubility curve for lime in solutions of phosphoric acid of lower concentrations than are given in the table, but owing to the length of time required to reach conditions of equilibrium and the analytical difficulties involved, the reliability of the results obtained was open to doubt and consequently this work was postponed for a separate investigation. Some idea as to the concentrations below which tricalcium phosphate might exist as a stable solid phase was, however, obtained.

A rather dilute solution of sodium phosphate, alkaline to litmus or phenolphthalein, was added to a dilute neutral solution of calcium chloride. After the addition of the first drop or two of the alkaline phosphate solution, the neutral calcium chloride solution became acid, and became more and more acid on further addition of the alkaline solution, as indicated by the color of the added litmus, up to a certain point, then gradually less and less acid, finally becoming alkaline. The points at which the maximum acidity was reached and at which the solution passed from acid to alkaline could not be sharply determined. The precipitated solid obtained by adding various amounts of the phosphate solution to a definite volume of the calcium chloride solution was always found to be dicalcium phosphate whenever the resulting supernatant solution possessed an acid reaction. When the supernatant solution was alkaline, however, the precipitate always contained a larger proportion of lime than is required by the formula for tricalcium phosphate. It became evident, therefore, that either tricalcium phosphate can exist under equilibrium conditions in contact with water over but a very narrow range of concentration or that it exists only as a metastable form in contact with water at room temperature, although the rate of change to a more stable form is probably quite slow.

The results given in the foregoing paragraphs have a special significance for agricultural investigations. It is generally held that monocalcium phosphate is the form contained in superphosphates or "acidulated" phosphates, and that the dicalcium phosphate is the salt of "reverted" phosphates. It is evident,

however, that no such concentration of the soil moisture with respect to phosphoric acid can be attained as is necessary for the continued existence of monocalcium phosphate, and that it must promptly and quite completely "revert" when added to the soil. It is obvious, therefore, that the relative values of the two phosphates as manures can not be entirely accounted for by the marked difference in their respective solubilities and consequent "availability," as has often been supposed.

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THE PHOSPHATES OF CALCIUM. II.[1]

BY F. K. CAMERON AND J. M. BELL.

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IN THE foregoing paper the equilibrium conditions in the system lime (CaO)–phosphoric acid (P_2O_5)–water, have been found for solutions which are comparatively quite concentrated with respect to both lime and phosphoric acid. It has been shown that for concentrations of P_2O_5 above 317 grams per liter the stable solid phase at 25° C. is monocalcium phosphate, and below that concentration down to 20 grams per liter the solid phase is dicalcium phosphate. The object of the present investigation was to find the equilibrium conditions for still lower concentrations of phosphoric acid and of lime and, especially in view of some preliminary experiments by Dr. Seidell, to find whether there might be a series of solutions, all of which can exist in equilibrium with tricalcium phosphate.

Several series of solutions were prepared by adding lime-water (Series M) or dicalcium phosphate (Series N) to solutions of phosphoric acid. The containing bottles were rotated in a constant temperature bath for about three months. After the analyses of the solutions had been made, it was found that between the end solutions of the foregoing paper and the most concentrated solutions of the present series there was a very large range for which there were no data. Another series (Series P) was prepared by adding dicalcium phosphate to somewhat more concentrated solutions of phosphoric acid than had been used in Series N. These solutions were rotated in the constant temperature bath

[1] Published by permission of the Secretary of Agriculture.

for about ten weeks during the past summer. The temperature, however, was often somewhat above 25° and it was impossible to keep it constant. Possibly for this reason, the solutions were somewhat richer in lime than would be expected from the extrapolated curve in the foregoing paper.

The method of analysis for lime and phosphoric acid has been recently given by Jarvinen.[1] The sample for analysis is added slowly to a boiling solution of oxalic acid and ammonium oxalate (10 cc. N ammonium oxalate and 5 cc. 2N oxalic acid diluted to 50 cc.), and then a 1 per cent. ammonia solution is added, drop by drop, to alkalinity. The precipitate of calcium oxalate is filtered, washed, dried, and ignited in the usual way. The filtrate is analyzed for phosphoric acid by the usual ammonium-magnesium phosphate method.

No correction was made for the small quantities of solution which adhered to the solid, and as the solutions were very dilute and were removed by means of suction this error is very small.

The results obtained from the several series are given in the following table:

COMPOSITION OF AQUEOUS SOLUTIONS OF LIME AND PHOSPHORIC ACID

No.	Series.	CaO per liter solution. Grams.	P_2O_5 per liter solution. Grams.	Ratio: P_2O_5/CaO in solid phase.
1	P	7.61.	19.96	1.3
2	P	6.51	16.52	1.2
3	P	5.01	12.82	1.3
4	P	3.42	8.16	1.3
5	P	2.42	5.75	1.2
6	P	1.58	3.66	1.2
7	N	0.544	1.516	1.2
8	N	0.400	1.108	1.1
9	N	0.291	0.773	1.1
10	N	0.232	0.662	1.1
11	N	0.145	0.381	1.0
12	M	0.062	0.109	0.9
13	M	0.049	0.088	0.9
14	M	0.034	0.015	0.8
15	M	0.587	0.013	0.4
16	M	0.789	0.012	0.4

The ratio of P_2O_5/CaO in dicalcium phosphate, $CaHPO_4$, is 1.27 and the first six solutions in the table evidently represent solutions in equilibrium with that solid. Solutions 7 to 14 inclusive are in equilibrium with a solid phase for which the ratio

[1] *Z. anal. Chem.*, **43**, 559 (1904).

P_2O_5/CaO varies from 1.17 to 0.85. The solid phases over this range are evidently solid solutions. Solution 14 contains only 15 parts per million of P_2O_5 and 34 parts per million of lime, and it will be noticed that the ratio P_2O_5/CaO in the solid phase is 0.85. This ratio for tricalcium phosphate $[Ca_3(PO_4)_2]$ is 0.84. Solutions 15 and 16 show markedly alkaline reactions to phenolphthalein, solution 13 an acid reaction, while solution 14 was almost neutral. Thus if lime-water is just neutralized with phosphoric acid and then if equilibrium conditions are obtained, the solid phase will be tricalcium phosphate or a solid solution of almost the same composition. The analytical methods are not delicate enough to determine whether there is a range of solution in equilibrium with tricalcium phosphate, although it may be stated that such a range would be extremely small in extent.

For very low concentrations of phosphoric acid there is quite a large quantity of lime in solution, while the solid phase here again is undoubtedly a solid solution. One of the solids comprising the first solid solution may safely be assumed to be dicalcium phosphate, but it is impossible to say what the other solid is. In the case of the second series of solid solutions one solid is lime. It may be, too, that there is only one series extending over the whole range, in which case the solids are dicalcium phosphate and lime.

Theoretically, there should be a point of intersection of the curve along which the solid is dicalcium phosphate and that along which the solid is the solid solution. At that point we should have present dicalcium phosphate, the solid solution of the limiting composition, liquid and vapor, and with the temperature fixed there would be an invariant point. It may be seen from the table that the composition of the limiting solid solution is quite close to that of dicalcium phosphate, and the analytical difficulties have made it impossible to determine the exact composition of the solid solution. The table shows, however, that the ratio P_2O_5/CaO in the limiting solid solution must be above 1.10 and below 1.27, and it shows that the composition of the liquid solution at that point lies between 0.40 and 0.54 gram CaO per liter, and between 1.11 and 1.52 grams P_2O_5 per liter.

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THE ACTION OF NITRATE OF SILVER ON DISODIUM ORTHOPHOSPHATE IN DILUTE SOLUTION.

By William Robert Lang and William Perot Kaufmann.

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The generally accepted text-book expression for the reaction which takes place between solutions of disodium orthophosphate and nitrate of silver is given as being

(1) $\underbrace{Na_2HPO_4}_{142.1} + \underbrace{3AgNO_3}_{509} = Ag_3PO_4 + 2NaNO_3 + HNO_3,$

indicating the complete precipitation of phosphoric acid as a silver salt and the setting free of nitric acid.

From the molecular weight in (1) it will be seen that 1 gram of disodium orthophosphate should react with 3.57 grams of silver nitrate.

In order to determine the correctness of this expression, decinormal solutions of these were made up and the phosphate titrated with the silver nitrate, using potassium chromate as an outside indicator. As the result of from 200 to 300 determinations it was found that the "end-point" of the reaction, as indicated by the first appearance of the red silver chromate, invariably occurred when an amount of silver solution had been added corresponding to the proportion of 1 gram of disodium orthophosphate to only 1.447 grams of silver nitrate. These proportions would indicate that a reaction had taken place as expressed by the equation

(2) $2Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + NaH_2PO_4 + 2NaNO_3.$

Ostwald, in his "Scientific Foundations of Analytical Chemistry" (second English edition, 1900), on page 204, gives this equation (2) as being probably the more correct expression of the reaction taking place between these substances, but adds that, ". . . . . it no doubt also fails to express all that goes on."

The analyses of types of the resulting silver phosphates may be tabulated as follows:

The figures in column (*e*) comparing the even with the odd, show that a greater yield of precipitate is obtained from the neutralized solutions than from those reacting acid, and a comparison of the yield of precipitate *obtained* and *calculated* in the case of the

TABLE I.

a. Reaction of solution.	*b.* Grams Na_2HPO_4 used.	*c.* Grams $AgNO_3$ used when "end-point" with K_2CrO_4 was reached.	*d.* "End-point" overstepped.	*e.* Grams precipitate yielded.	*f.* Calculated yield of precipitated Ag_3PO_4 from grams $AgNO_3$ in columns *c* and *d*.	*g.* Calculated yield from grams Na_2HPO_4 in column *b*.	*h.* Grams Na_2HPO_4 not acted on by $AgNO_3$.	*j.* Percentage of silver in precipitated phosphates.
(1) Acid	0.7105	1.17872	.....	0.9608	0.9700	2.09	0.4 (=57%)	76.96
(2) Neutralized by dilute KHO	0.7105	1.17872	.....	0.9655	0.9700	2.09	0.4 (=57%)	75.82
(3) Acid	0.7105	.....	1.696 (excess)	1.0630	1.734	....	.....	76.19
(4) Neutralized by dilute KHO	0.7105	.....	1.696 (excess)	1.4070	1.734	....	.....	76.80
(5) Acid	0.7105	.....	2.544 (large excess)	1.1350	2.601	....	.....	76.65
(6) Neutralized as No. 4	0.7105	.....	2.544 (large excess)	2.3841	2.601	....	.....	77.36

neutralized solution makes it evident that even in such menstrua the phosphate enters appreciably into solution.

It will be seen from (1) and (2), which are typical of a large number of determinations, that the "end-point" occurs at a stage in the reaction where only a partial separation of the phosporic acid as the silver salt has taken place. The resulting solution is acid to litmus, which acidity is due to the dihydrogen sodium orthophosphate; no free nitric acid could in any case be detected at this stage. It is evident, however, from these determinations and from Nos. 3, 4, 5 and 6 that equation (2) only expresses accurately what takes place when silver nitrate is added to disodium orthophosphate and the completion of the reaction taken as being indicated by the first formation of argentic chromate.

As from these results it was evident that there remained a considerable quantity of phosphoric acid in combination as (presumably) dihydrogen sodium orthophosphate, silver nitrate was added in excess to effect its complete precipitation, if possible, and the precipitates analyzed. The results are expressed in percentages of silver which was determined first of all gravimetrically, but later on Volhard's method was substituted on account of the close agreement of the gravimetric estimations. The only one of the percentages in column (*j*) which *accurately* corresponds to the substance Ag_3PO_4 is No. 6, the others showing a deficiency in their silver content of from 0.4 to 1.54 per cent. But in the earlier stages of this investigation in four cases precipitates were obtained which yielded, on analysis, respectively:

	Silver. Per cent.
(1) "End-point" reaction.....	73.76
(2) "End-point overstepped	74.19
(3) Large excess of silver nitrate.....	73.88
(4) Deficiency of silver nitrate..... ...	73.62
Average.....	73.862

These precipitates evidently correspond exactly to the formula $Ag_5H(PO_4)_2$ which contains 73.86 per cent. of silver. The others in Table I, numbered (1) to (5), lie between somewhere Ag_3PO_4 with 77.32 per cent. and $Ag_5H(PO_4)_2$ with 73.86 per cent. of silver.

The following table contains the percentage of silver found in a number of precipitates obtained under similar conditions of temperature and concentration, but in different total quantities

of the reacting salts. We have found it so far impossible to produce at will the phosphate of any desired composition but hope that further investigation will enable us to accomplish this.

TABLE II.—SILVER CONTENT IN PERCENTAGES.

73 per cent. and below 74 per cent.	75 per cent. and below 76 per cent.	76 per cent. and below 77 per cent.	77 per cent. and above.
73.49	75.34	76.47	77.01
	75.23	76.17	
	75.95	76.77	
	75.01	76.47	
	75.78	76.25	
		76.70	
		76.43	
		76.52	
		76.35	
		76.82	
		76.57	
		76.96	
		76.25	
		76.23	

It will be seen from this that the most commonly occurring precipitates nearly approach that of the composition Ag_3PO_4 *but not quite.*

Having obtained the "end-point" with potassium chromate (the reaction expressed by

$$2Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + NaH_2PO_4 + 2NaNO_3),$$

and having filtered off the precipitate, an excess of silver nitrate was added, causing further precipitation of a phosphate containing 76.25 per cent. to 76.5 per cent. of silver. The filtrate from this further precipitate was found to contain free nitric acid and also responded to tests for phosphoric acid. Following the equation given above, it would seem that the dihydrogen sodium phosphate reacted further with the silver nitrate possibly in accordance with the following equations:

(3) $$NaH_2PO_4 + AgNO_3 = AgH_2PO_4 + NaNO_3,$$

(4) $$AgH_2PO_4 + AgNO_3 = Ag_2HPO_4 + HNO_3,$$

(5) $$Ag_2HPO_4 + AgNO_3 = Ag_3PO_4 + HNO_3.$$

Combining these equations there would be obtained the expression

(6) $$NaH_2PO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3,$$

which does not account for the presence of phosphoric acid in

the filtrates; but if (4) and (5) are coupled, the precipitate will have the composition $Ag_5H(PO_4)_2$ which was obtained in the four cases previously quoted, the production of which can be expressed by the equation

(7) $$2Na_2HPO_4 + 5AgNO_3 = \underbrace{Ag_5H(PO_4)_2}_{Ag_3PO_4.Ag_2HPO_4} + 4NaNO_3 + HNO_3.$$

For an expression which would account for the presence in the filtrate from the complete (?) precipitation of the silver, of both nitric acid and of phosphoric acid the following is suggested:

(8) $4Na_2HPO_4 + 6AgNO_3 = 2Ag_3PO_4 + 4NaNO_3 + HNO_3 + H_3PO_4$

It would appear then that the reaction between silver nitrate and disodium orthophosphate takes place in several distinct stages, and that the formation of a phosphate containing about 76 per cent. of silver is the most constant resultant. Also that free nitric acid and phosphoric acid remain in the solution from which no further precipitate can be obtained on the addition of the nitrate. It is our intention to further investigate this matter specially as regards the quantitative composition of these filtrates with a view to determining whether or not the last six equations suggested (Nos. 3 to 8) adequately express the reaction.

THE CHEMICAL LABORATORIES,
THE UNIVERSITY OF TORONTO.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE, NO. 59.]

A CONSTANT TEMPERATURE BATH FOR LOW TEMPERATURES.

BY A. GIVEN.

Received October 12, 1905.

THE usual temperature at which specific gravity determinations are made is 15.6° C. (60° F.), and it was for this temperature that this bath was primarily intended, and at which the bath has been used, though modifications of it are in use at 20° C. The advantage of such a bath lies in the fact that the whole body of the pycnometer is immersed, after cooling to 14° C. or below, and therefore rises to the desired temperature more quickly and uniformly than in any other way. Moreover, the pycnometer can be left in the bath as long as may be desired without change

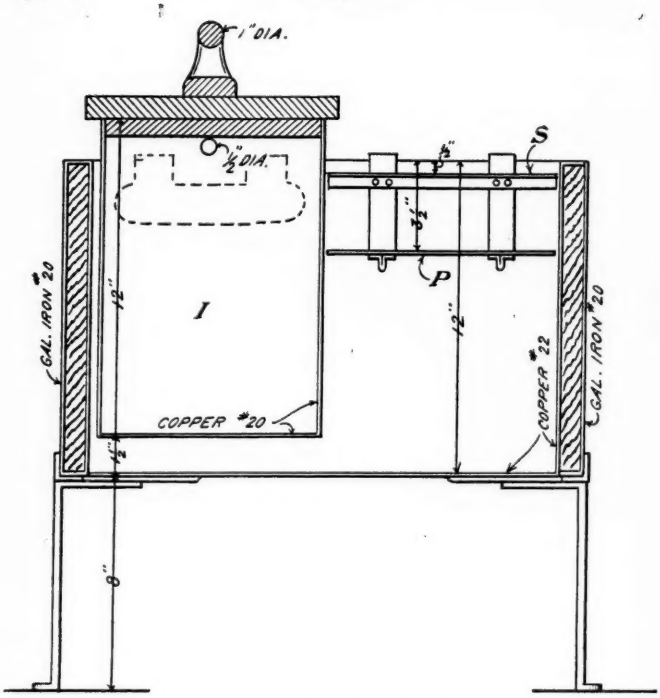


Fig. 1. Section on line A–B.

of temperature. Being held at such a relatively low temperature, the loss by evaporation is reduced to a minimum, and no appreciable change occurs in the density of the solution. The bath was built for the Bureau by a local tinsmith at a cost of $22.00. The construction is shown in the drawing.

The apparatus consists of a double-walled bath, of which the inner wall and bottom are of copper, and the outside of galvanized iron, and a suitable stand. The space between the walls of the bath is packed with asbestos in order to insulate the contents of the bath as far as possible. In the bath is the copper ice-box *I*, of the same depth as the bath, extending to within $1^1/_2$ inches of the bottom, and raised that much above the top of the bath to provide an overflow for the waste water from the melting ice. The wooden cover serves as an insulator. The remaining space in the bath is taken up by the perforated shelf

P, which is fixed at the proper depth for the pycnometers or other vessels used. Above this, and fastened to the same hangers, is the narrow shelf *S*, which carries the thermometer and gas regulator. This regulator (Fig. 4) which was designed and made by Mr. B. J. Howard, of the Bureau of Chemistry, is one of the most necessary

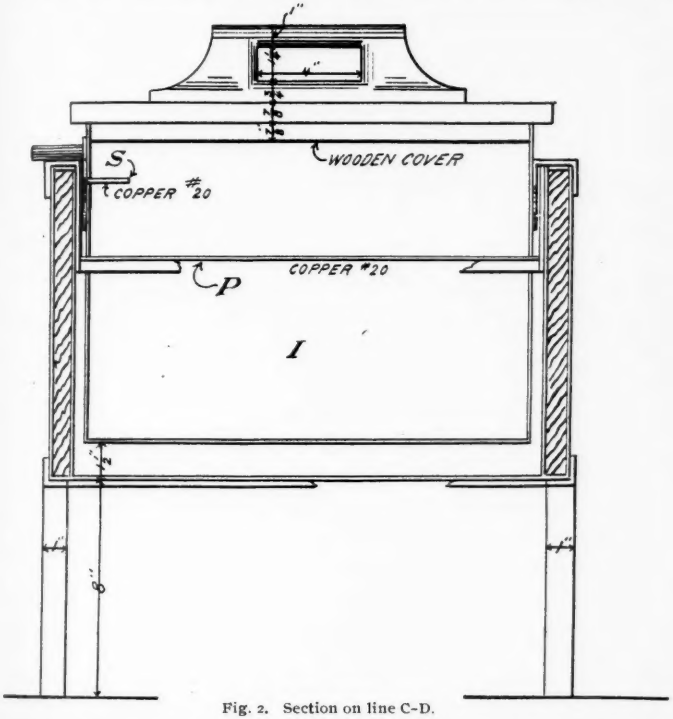


Fig. 2. Section on line C-D.

parts of the apparatus, as it is the sensitiveness of the regulator which has contributed so much to the constancy of the temperature of the bath. The large bulb, 1 inch in diameter and 5 inches long, is filled with methyl alcohol, though toluene, having a higher coefficient of expansion, would perhaps be better. The regulator is connected with the gas supply, and with a Bunsen burner so adjusted that it will not strike back when the gas supply is nearly cut off. For maintaining an equal temperature throughout the bath some form of stirrer is necessary, and we have used with good results

a gentle current of air, conducted to the bottom of the bath close beside the ice-box.

In starting the bath, the ice-box is first filled with water, and the rest of the bath with distilled water. Large pieces of ice are then placed in the ice-box. The stirrer is started, and to lower the temperature still faster, a clean piece of ice is placed on

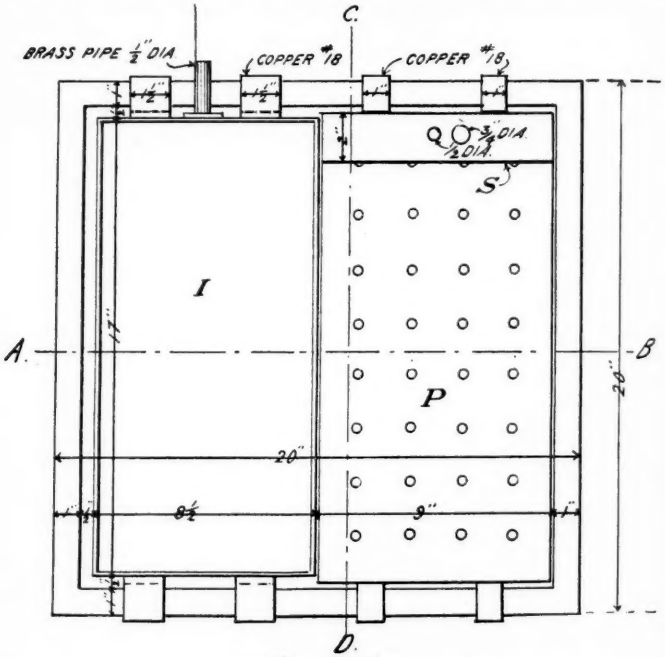


Fig. 3. Top view.

the platform. When the thermometer shows that the temperature is about to fall below the desired point, the gas is turned on, and the piece of ice removed from the platform. A bath 18 inches square and 12 inches deep uses, in the hottest weather, about fifty pounds of ice in seven hours. As long as there are 300 or 400 grams of ice in the box, the temperature will remain constant, and if the ice-box is kept supplied, the thermometer shows no change of temperature for hours at a time. It is necessary to have a large volume of water in the bath in order that the temperature may not be affected by putting in and taking out the pycnometers.

The following table gives the results of ten duplicate determinations of specific gravity on samples of whiskey. The tem-

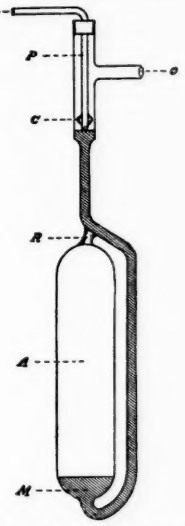


Fig. 4. Temperature regulator: *I*, gas inlet; *O*, gas outlet; *P*, pilot flame supply; *C*, centering knobs of glass; *R*, rod of glass to strengthen the apparatus; *A*, alcohol reservoir; *M*, mercury trap.

perature at which the filling of the pycnometers was made remained constant at 15.6°.

Serial number.	Specific gravity.
14772	0.91139
	0.91136
14773	0.90820
	0.90804
14794	0.94395
	0.94395
14805	0.91148
	0.91141
14806	0.91274
	0.91275
14814	0.94021
	0.94020
14842	0.94099
	0.94095
15005	0.94090
	0.94085
15006	0.94218
	0.94214
15007	0.94023
	0.94017

It will be readily seen that the application of this bath is not confined to specific gravity determinations. At the same time that the one here described was built, another of the same surface area, but 22 inches deep, was constructed for use with the Roese fusel oil apparatus, which must be kept at constant temperature in order to get comparative results. Later, another, slightly smaller than the one described, was ordered for use with the Zeiss immersion refractometer. This has a basket of galvanized wire, bound with copper, instead of the perforated plate. The part of this basket next the ice-box is divided into compartments for holding four flasks. In front of these compartments is a strip of copper with holes for the small beakers used with the refractometer, under which is the strip of ground glass through which the light passes upwards. The wire frame for supporting the instrument is fastened to the sides of the basket, and the mirror for directing the light upward is attached below. The bath itself differs from those previously made in that the front side is of glass, to permit the entrance of light. This bath is kept at 20° C., and works just as perfectly as the one at 15.6° C.

The writer acknowledges suggestions from Messrs. Tolman, Howard and Munson, of this Bureau.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 98.]

THE RAPID PRECIPITATION OF ANTIMONY IN THE ELECTROLYTIC WAY.

BY JULIA LANGNESS AND EDGAR F. SMITH.

Received August 28, 1905.

THE BEST electrolyte for the determination of antimony is sodium sulphide, containing a small amount of sodium hydroxide. The polysulphides, frequently present, have been destroyed in various ways, one of the most convenient being by the addition of potassium cyanide, first used by A. Fischer,[1] and subsequently and wholly independently by Exner,[2] when describing his experiences in the rapid determination of metals with the aid of a rotating anode. His results in the case of antimony were exceedingly good, both from the point of rapid and complete pre-

[1] *Ber.*, **36**, 2348.

[2] This Journal, **25**, 896.

cipitation of the metal as well as from the appearance of the deposit. Nevertheless, there seem to have been some difficulties encountered by other experimenters[1] upon repeating Exner's work with this metal, so that we have thought it only proper to communicate the observations made by us with the same metal during the past summer.

To begin, let it be noted that the antimony was present in solution both in its trivalent and quinquivalent form. Whichever compound it happened to be was weighed out and dissolved in a definite amount of sodium sulphide, diluting, of course, to a specified volume from which portions were removed for electrolysis. In this way a solution was prepared so that 10 cc. of it contained 0.2405 gram of antimony. Several such portions were treated as follows: to each were added 15 cc. of sodium sulphide (sp. gr. 1.18), 3 grams of potassium cyanide, 1 cc. of sodium hydroxide (10 per cent.), the solution was diluted to 70 cc. with water, heated almost to boiling and electrolyzed.

EXPERIMENTS.

No.	Volts.	N. D_{100} Amperes.	Time. Minutes.	Antimony found. Gram.
1.....	3.5 to 4	6	15	0.2404
2.....	3.5 to 4	6	15	0.2409
3.....	3.5 to 4	6	15	0.2410
4.....	3.5 to 4	6	15	0.2402
5.....	3.5 to 4	6	15	0.2402

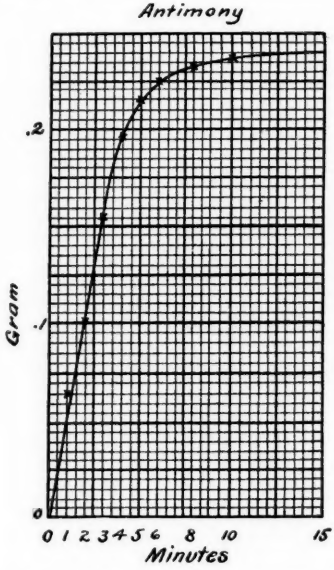
The precipitation was complete in each instance. The deposits of antimony were bright gray in color, like those of zinc. They were also perfectly adherent, exhibiting no signs of sponginess. Indeed, by employing roughened dishes as cathodes as much as 0.4851 gram and 0.4847 gram, and even 1 gram of metal were deposited in a beautiful and perfectly compact form in from twenty to twenty-five minutes. With conditions similar to those described above, experiments were conducted in a smooth platinum dish as cathode to ascertain the rate of precipitation. Thus, with a current of 6.5 amperes and 3.5 volts:

0.0652 gram of antimony was deposited in one minute,
0.1007 gram of antimony was deposited in two minutes,
0.1575 gram of antimony was deposited in three minutes,
0.1969 gram of antimony was deposited in four minutes,
0.2140 gram of antimony was deposited in five minutes,

[1] Fischer and Boddaert: *Z. f. Elektrochemie*, **10**, 950.

0.2251 gram of antimony was deposited in six minutes,
0.2331 gram of antimony was deposited in seven minutes,
0.2369 gram of antimony was deposited in eight minutes,

and fifteen minutes for the entire amount of metal. These values gave the following curve:



Numerous experiments having been performed to subject the method to the most varying conditions, it was concluded to try it in the analysis of the mineral stibnite. Very pure samples of the latter were reduced to powder, and 0.5-gram portions were digested with 20 cc. (or more) of sodium sulphide (sp. gr. 1.18), filtered from the insoluble part, and after adding 3 grams of potassium cyanide and 1 cc. of sodium hydroxide to the solution the latter was heated to boiling and electrolyzed. Two results will suffice to show the applicability of the method.

Expt.	Mineral. Gram.	Volts.	Amperes.	Time.	Antimony. Gram.	Antimony. Per cent.
1.....	0.4241	3	7	25	0.3015	71.09
2.....	0.4488	3	7	20	0.3174	70.72

The deposits were all that could be desired. The residues contained no antimony. From a careful observation of the

method it may be added that the omission of the 1 cc. of sodium hydroxide from the electrolyte works no harm. The volume of sulphide may be reduced to 10 cc. without affecting the result; but then the quantity of alkaline cyanide should be reduced to 2 grams. The reduction of the cyanide to 1 gram without a corresponding reduction of sulphide is apt to give rise to a black border upon an otherwise most satisfactory deposit. If the volume of the alkaline hydroxide be increased to 10 cc., the antimony deposit will be black, powdery and non-adherent.

SEPARATION OF ANTIMONY FROM ARSENIC.

This separation can be carried out with perfect satisfaction when using the rotating anode. The conditions observed in getting the results given below were as follows: A solution of antimony oxychloride in sodium sulphide was made so that 10 cc. of it contained 0.1268 gram of antimony, and to each such portion were added 15 cc. of sodium sulphide (sp. gr. 1.18), 3 grams of potassium cyanide and water to increase the volume of liquid to 70 cc. On applying a current of 6 amperes and 4 volts the antimony was completely precipitated in from fifteen to twenty minutes.

RESULTS.

0.1268 gram of antimony.
0.1267 gram of antimony.
0.1269 gram of antimony.
0.1267 gram of antimony.
0.1269 gram of antimony.
0.1268 gram of antimony.

The deposit of metal was in each instance beautiful, light gray in color, metallic, and perfectly adherent. The arsenic existed in the solution as a sulpharsenate = (0.2000 gram of arsenic).

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 99.]

THE USE OF THE ROTATING ANODE AND MERCURY CATHODE IN ELECTRO-ANALYSIS.

BY LILY G. KOLLOCK AND EDGAR F. SMITH.

Received October 13, 1905.

(SECOND PAPER.)

IN THE previous communication upon this subject zinc, copper, nickel, cobalt, chromium and iron were the metals precipitated

under widely varying conditions with such completeness and surprising rapidity that it was concluded to include still other metals within the scope of the study before turning to an inquiry into certain side reactions, observed from time to time, which tended to draw attention to themselves. These, though most attractive and persistent in their appearance, must remain for more careful and thorough study in the future. Indeed, the side problems in electro-analysis, thus constantly obtruding themselves, have too long been neglected; they call for attention. Their solution will surely solve difficulties encountered by the analyst; remove serious doubts and pave the way for a wider introduction and constant use of the methods of electro-analysis. But, turning to the thought which prefaced this communication, other metals in the form of sulphates were carefully investigated. The results appear in the subjoined paragraphs.

CADMIUM.

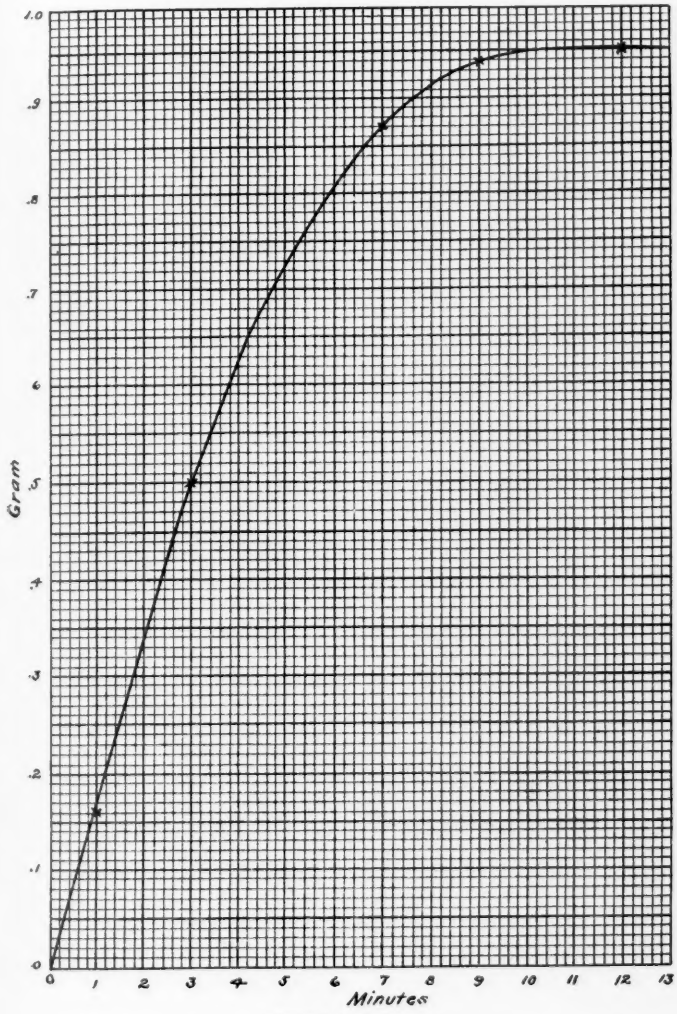
Reference to the literature[1] pertaining to the electrolytic determination of this metal will show that this method of estimating it is in every way superior to the ordinary gravimetric procedures. And only recently Miss Davison, working in this laboratory, has recorded the best electrolytes and the most satisfactory conditions for its estimation with a rotating anode and platinum cathode. To this helpful contribution it is desired to add the data derived from the use of a mercury cathode, supplemented with a rotating anode. The decomposition tube, of the size and arranged as heretofore described, contained from 60 to 70 grams of mercury. Upon this were placed 5 cc. of an aqueous solution of cadmium sulphate, equivalent to 0.9480 gram of metallic cadmium. The current acting upon this solution registered from 1.5 to 3.5 amperes and 10 to 7 volts. It was interrupted at the end of fifteen minutes. The liquid, siphoned from off the mercury, did not show the presence of any cadmium upon the addition of hydrogen sulphide. The metal had entered the mercury completely, the resulting amalgam having much the appearance of zinc amalgam except that it was brighter in color. The anode made 360 revolutions per minute.

The rate of precipitation of the cadmium was as follows:

0.1531 gram in one minute.

0.4984 gram in three minutes.

[1] Smith's "Electrochemical Analysis," p. 68.



Curve I. Cadmium.

0.8707 gram in seven minutes.
0.9480 gram in nine minutes.
0.9484 gram in ten minutes.

A trace of metal was found in the liquid from the nine-minute experiment, but absolutely none in that from the ten-minute trial. The time (Curve I, page 1529) was drawn from these last results.

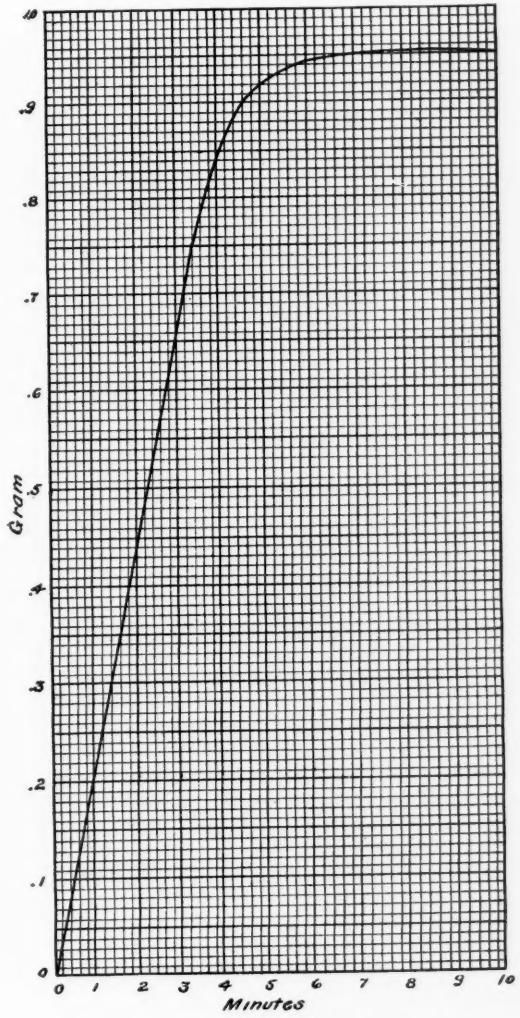
As acid was not added to the electrolyte at the start, the current did not exceed 1 ampere, but with the liberation of acid from the salt the current quickly rose to 3.5 amperes, and this strength was maintained in all the subsequent precipitations. Thus, with these conditions, the following quantitative precipitations were made:

Cadmium found. Gram.	Time. Minutes.
0.9480	15
0.9480	10
0.9484	15
0.9481	12
0.9478	12
0.9478	12
0.9479	10
0.9479	10

The quantity of metal present in each determination was 0.9480 gram. Maintaining thus a current of definite strength throughout the decomposition, it next became an object to ascertain the rate of precipitation of metal under such conditions. Accordingly, 5 drops of concentrated sulphuric acid (40 drops equal 1 cc.) were added to 5 cc. of a cadmium sulphate solution, containing 0.9480 gram of metal, and electrolyzed with a current of 3.5 amperes and 10 to 7 volts:

In three minutes 0.6472 gram of cadmium was deposited.
In five minutes 0.9389 gram of cadmium was deposited.
In seven minutes 0.9478 gram of cadmium was deposited.
In ten minutes 0.9477 gram of cadmium was deposited.
In twelve minutes 0.9481 gram of cadmium was deposited.
These data gave Curve II (page 1531).

The liquid poured off from the mercury in the seven-minute period showed only the slightest yellow tinge when it was treated with hydrogen sulphide. Other trials conducted with conditions similar to those first mentioned gave these results in metallic



Curve II. Cadmium.

cadmium: 0.9484, 0.9479, 0.9478, 0.9477, 0.9483, 0.9481, 0.9484 gram.

To learn the time necessary to precipitate smaller quantities of metal, a solution was made up containing 0.1600 gram of cadmium in 5 cc. On acting upon this last volume with a current of 3.5 amperes and 7 to 4 volts, the entire quantity of metal (0.1600 gram) was completely precipitated in three minutes. The following rates of deposition are shown in Curve III:

In one minute 0.1370 gram of cadmium was deposited.
In two minutes 0.1577 gram of cadmium was deposited.
In three minutes 0.1602 gram of cadmium was deposited.
In four minutes 0.1596 gram of cadmium was deposited.

Other results, obtained in three minutes, showed cadmium as follows: 0.1598, 0.1600 and 0.1601 gram.

The rate of deposition of metal from a solution, containing 0.3250 gram of cadmium in 5 cc., was also studied with these results:

In one minute 0.1945 gram of metal was deposited.
In two minutes 0.2835 gram of metal was deposited.
In three minutes 0.3150 gram of metal was deposited.
In four minutes 0.3217 gram of metal was deposited.
In five minutes 0.3249 gram of metal was deposited.

Cadmium was found in the residual liquor from Expt. 4, but absolutely none in that from the fifth experiment.

The preceding results gave Curve IV. From a solution containing 0.4740 gram of cadmium all of the metal was precipitated in five minutes:

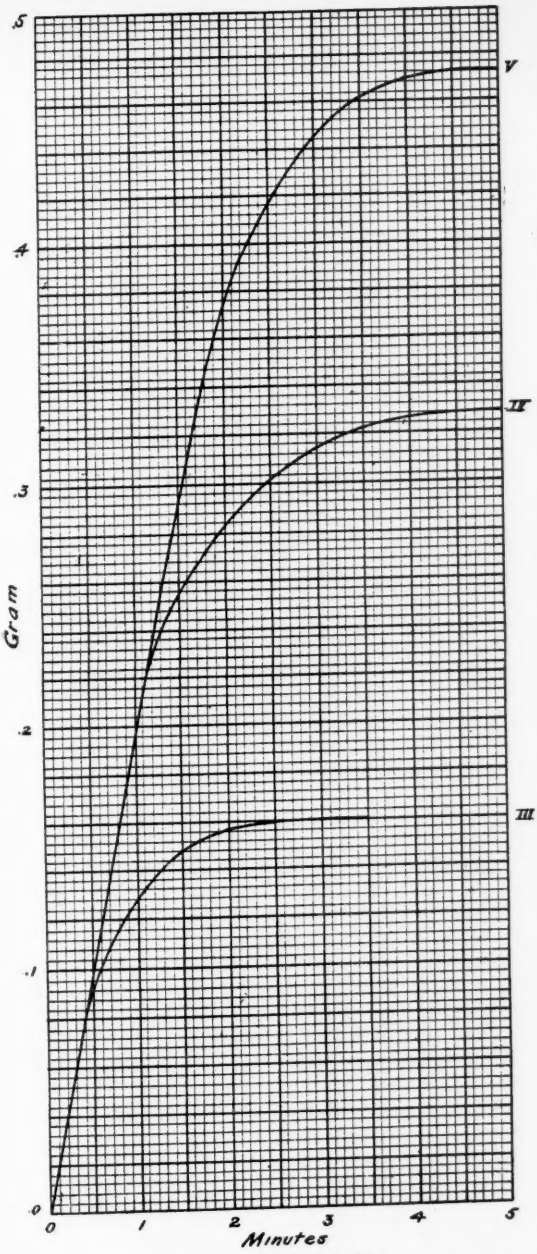
In one minute 0.3706 gram was deposited.
In three minutes 0.4633 gram was deposited.
In five minutes 0.4743 gram was deposited.

Curve V was deduced from these figures.

The addition of 20 drops of sulphuric acid (or 0.5 cc.) to the solution, retaining the current conditions previously mentioned, produced no ill effect as 0.1591 gram of cadmium, instead of 0.1600 gram, was precipitated in three minutes. One cubic centimeter (40 drops) of concentrated acid, however, retarded the deposition, since only 0.1507 gram of metal was thrown down into the mercury in three minutes.

TIN.

While this metal has been determined quite often in the elec-



Curves III, IV, V.—Cadmium.

trolytic way the method does not appear to have gained such recognition as it justly deserves. It was thought that it would be well to learn how its solutions deported themselves when electrolyzed under the conditions prevailing in this and the previous communication to which it serves as a sequel. Accordingly, stannous hydrate was dissolved in sulphuric acid, the solution being so made up that 5 cc. of it contained 0.4106 gram of metallic tin and 0.2 cc. of concentrated sulphuric acid. A current of 2 to 4 amperes and 5 to 4 volts acted for ten minutes upon 5 cc. of this solution. The mercury increased 0.4109 gram in weight and the liquid poured off from it showed no tin upon examination. The addition of sulphuric acid seemed in no way to arrest the precipitation of metal, for the following masses of it were obtained with a current of 4 amperes and 5 volts:

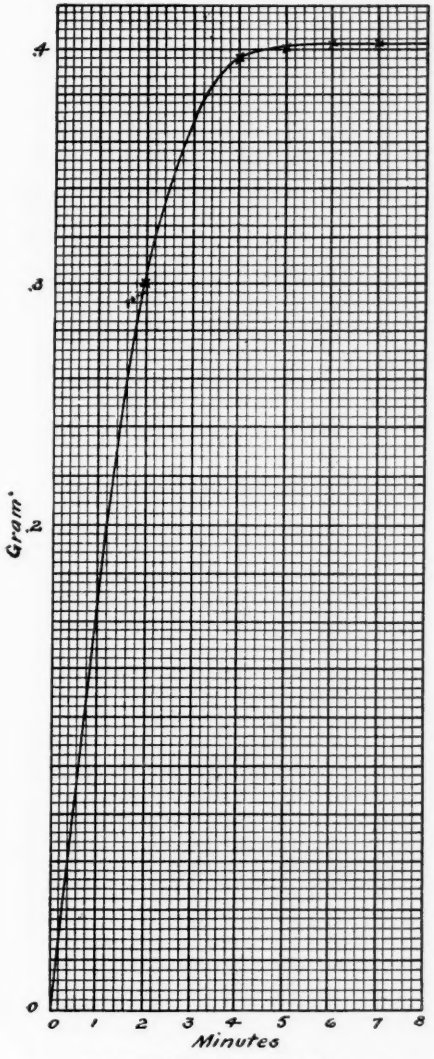
In two minutes 0.2898 gram.
In four minutes 0.3890 gram.
In five minutes 0.4068 gram.
In six minutes 0.4106 gram.
From them Curve VI was drawn.

Even in the presence of a smaller amount (0.5 cc.) of acid, almost identical results were obtained:

In two minutes 0.2997 gram of tin was deposited.
In four minutes 0.3974 gram of tin was deposited.
In five minutes 0.4060 gram of tin was deposited.
In six minutes 0.4106 gram of tin was deposited.

It was found advantageous to let the solution heat up quietly in order that the condensed steam might wash down the sides of the tube, otherwise traces of basic sulphate separated on the walls of the decomposition cell. With a current of 5 amperes and 5 to 4 volts it was possible to precipitate 0.8212 gram of tin (10 cc. of solution) in eight minutes.

Experiment.	Tin present. Gram.	Sulphuric acid. Volume. cc.	Sulphuric acid. cc.	Current. Amperes.	Volts.	Time. Minutes.	Tin found. Gram.	Error. Gram.
1	0.4106	5	0.2	2–4	5	10	0.4109	+0.0003
2	0.4106	5	0.2	4	5	9	0.4114	+0.0008
3	0.4106	5	0.2	4	5–4.5	9	0.4109	+0.0003
4	0.4106	6	0.5	4	5	6	0.4106	.....
5	0.4106	5	0.25	4	5	6	0.4106	.....
6	0.8212	10	0.5	6	5.5	9	0.8210	—0.0002
7	0.4106	10	0.75	5	5	8	0.4107	+0.0001
8	0.4106	7	0.05	5	5	7	0.4106	.....
9	0.4106	7	0.25	5	5	10	0.4107	+0.0001

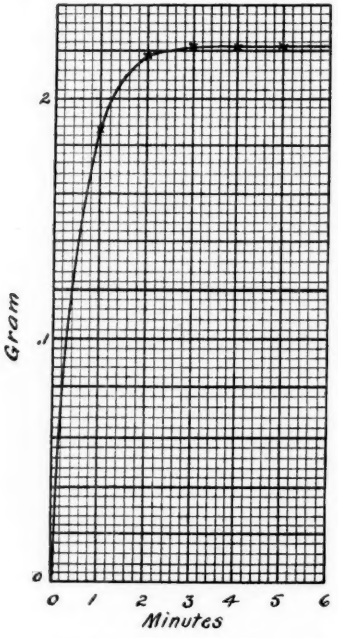


Curve VI. Tin—4 amperes, 5 volts.

SILVER.

There is nothing really to be added to the electrolytic methods proposed for this metal, and it would perhaps not have been included in our experiments had not the question arisen—as to whether nitrates could be used with a mercury cathode, the thought being that possibly they might be reduced to ammonia and the latter then enter the mercury. But the electrolysis of nitric acid and nitrates under the conditions prevailing in the experiments here recorded, *viz.*, with high current density and voltage, never resulted in this way, and, therefore, enables the analyst to employ this class of salts in metal determinations with a mercury cathode and rotating anode. In confirmation of these statements silver, mercury and bismuth nitrates were thus electrolyzed and the results therefrom are given in the succeeding paragraphs.

The conditions observed with silver nitrate were:



Curve VII. Silver—4 amperes, 6 volts.

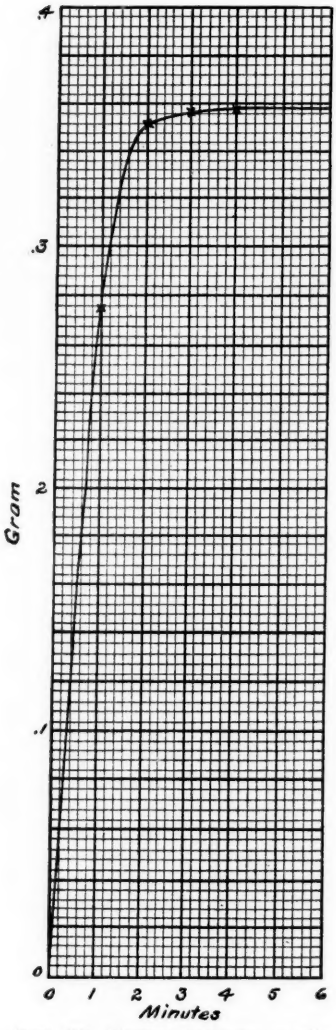
Volume of solution, 5 cc. (equal to 0.2240 gram of Ag).
Nitric acid 5 drops (30 drops equaled 1 cc.).
Current, 4.5 to 3 amperes.
Volts, 6.5 to 6.
The anode made 1200 revolutions per minute.
Results:
In one minute 0.1874 gram of silver was deposited.
In two minutes 0.2178 gram of silver was deposited.
In three minutes 0.2207 gram of silver was deposited.
In four minutes 0.2240 gram of silver was deposited.
These gave Curve VII.

As might be expected, working with a nitric acid solution, there was an anodic deposit. At the end of one minute this was quite heavy but when two minutes had expired it was almost entirely gone, and in three minutes the anode was perfectly clean. Silver is precipitated quite rapidly, hence the anode was given high speed to insure agitation of the mercury and thereby render the silver absorption more rapid. It is not advantageous to have a greater concentration than 0.3500 gram of silver in 5 cc.

Experiment.	Silver present. Gram.	Volume. cc.	Nitric acid in drops. 30=1 cc.	Current. Amperes.	Volts.	Revolutions of anode per minute.	Time. Minutes.	Silver found. Gram.	Error. Gram.
1	0.2240	5	5	1	6	1400	7	0.2240	.....
2	0.2240	5	5	3-5	6-5	1360	5	0.2241	+0.0001
3	0.2240	5	5	4-2	6-5	1360	5	0.2246	+0.0006
4	0.2240	5	2	3-2.5	7-6	1360	5	0.2236	—0.0004
5	0.2240	5	5	4.5-3	6.5-6	1200	4	0.2240	.....
6	0.2240	5	1	3-2	5-4	200	5	0.2238	—0.0002
7	0.4480	10	5	2.5	5.5	1200	8	0.4472	—0.0008
8	0.2240	5	5	2.5	5.75	1080	5	0.2244	+0.0004
9	0.4480	10	10	3.5	6	1440	6	0.4471	—0.0009
10	0.4480	10	5	3.5	6	1440	6	0.4475	—0.0005
11	0.3720	5	2	2.5-3	8-6	1200	5	0.3719	—0.0001
12	0.3720	5	3	2.5-3	8-6	1200	4	0.3723	+0.0003
13	0.3720	5	10	3	8	1200	5	0.3713	—0.0007

MERCURY.

A solution of mercurous nitrate was used. It contained 0.3570 gram of mercury in 5 cc. Sufficient nitric acid was also present to prevent the formation of a basic salt. A current of



Curve VIII. Mercury—3 amperes, 7-5 volts.

3 amperes and 7 to 5 volts decomposed the salt at the following rate:

In one minute 0.2777 gram of mercury was deposited.
In two minutes 0.3542 gram of mercury was deposited.
In three minutes 0.3572 gram of mercury was deposited.

Curve VIII was constructed from these values.

The effect of dilution upon the rate of deposition was learned by adding water to 5 cc. of the solution just mentioned until its volume became 25 cc. It was then exposed to a current of 3 amperes and 13 to 7.25 volts. When it was found that eight minutes were necessary to completely precipitate the metal present, the masses deposited were:

In two minutes 0.2796 gram of mercury,
In five minutes 0.3488 gram of mercury,
In seven minutes 0.3552 gram of mercury,
In eight minutes 0.3570 gram of mercury,

from which was constructed Curve IX.

It was found that the addition of free nitric acid tended to retard the rate of precipitation unless the pressure was maintained at 5.5 volts, the current strength sometimes then rising to 8 amperes. Even in the presence of 1 cc. of the acid all of the mercury was deposited in three minutes:

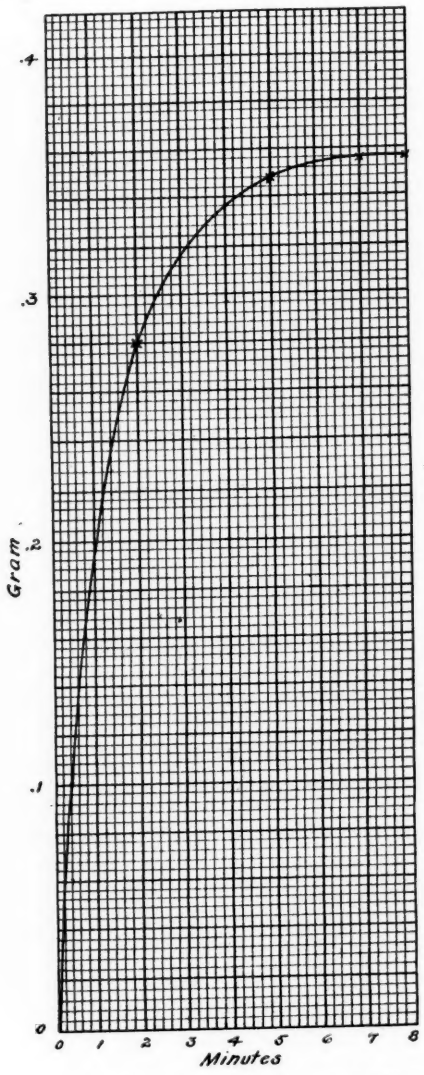
In two minutes 0.3498 gram of mercury.
In three minutes 0.3569 gram of mercury.
In four minutes 0.3569 gram of mercury.

The total quantity of mercury present equaled 0.3575 gram.

Experiment.	Mercury present. Gram.	Volume.	Nitric acid. cc.	Current. Amperes.	Volts.	Time.	Mercury found. Gram.	Error. Gram.
1	0.3575	5	0.02	3	7–5	4	0.3576	+0.0001
2	0.3575	5	0.02	3	7–5	3	0.3572	+0.0003
3	0.3575	5	0.02	3	7–5	4	0.3573	+0.0002
4	0.3575	5	0.02	3	7–5	3	0.3573	+0.0002
5	0.3575	5	0.02	3	7–5	3	0.3566	—0.0001
6	0.3575	5	0.02	3	7–5	3	0.3574	+0.0001
7	0.3575	25	0.02	3	13–7.25	8	0.3575	.....
8	0.3575	6	1	8–7	5.5	4	0.3569	—0.0006
9	0.3575	6	1	8–7	5.5	3	0.3569	—0.0006

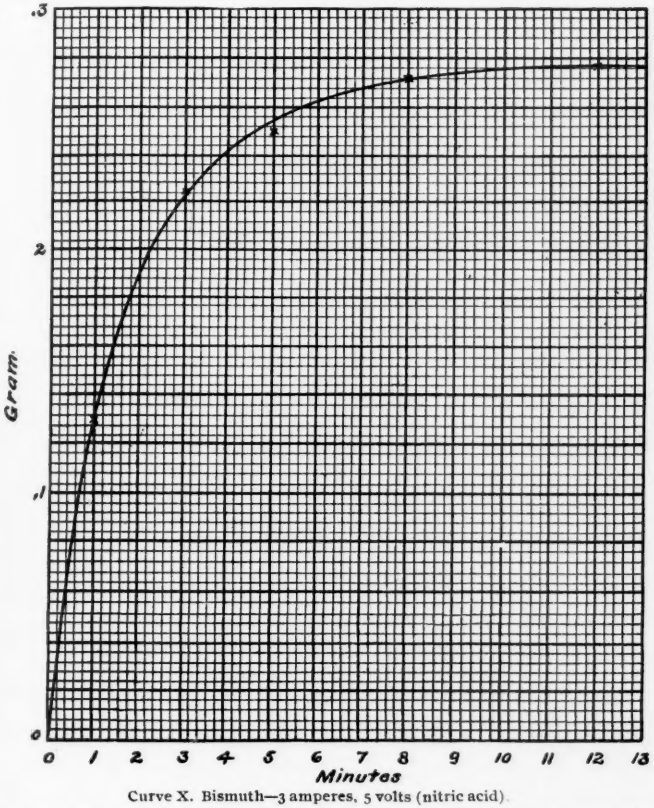
BISMUTH.

This metal, as is well-known, has always presented difficulties when determined electrolytically, so that the successful conditions which have been offered must be strictly observed in order



Curve IX. Mercury—25 cc.—3 amperes, 13-7 volts.

that the results may be satisfactory. The formation of peroxide on the anode simultaneously with the precipitation of metal on the cathode has been the problem. To prevent the anodic deposit has called forth numerous suggestions which need not be given here. The addition of a glycerol mixture did not entirely

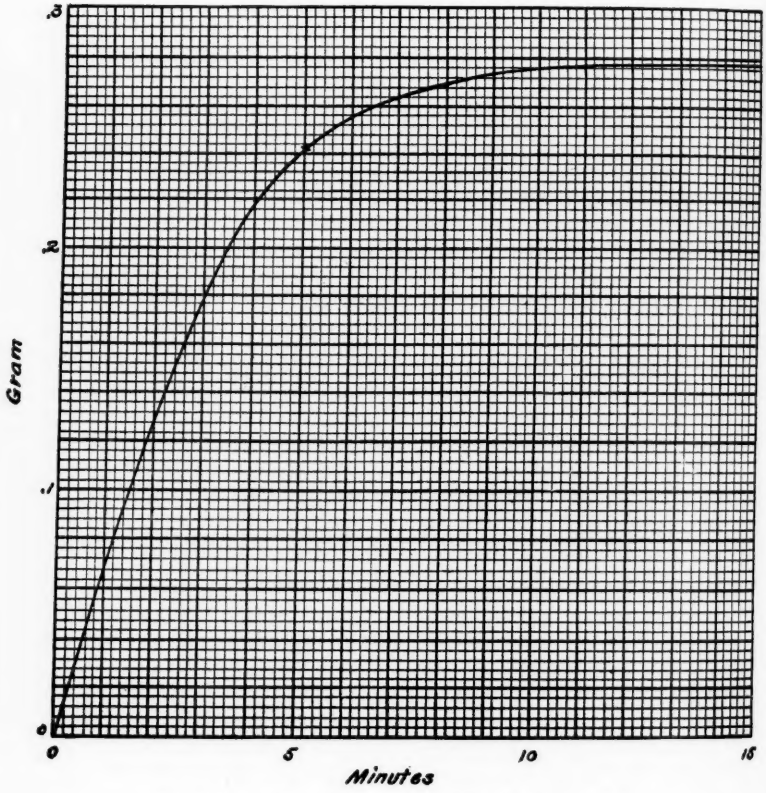


Curve X. Bismuth—3 amperes, 5 volts (nitric acid).

prevent the peroxide formation, nor did the reduction of the current, after it had acted awhile, produce the beneficial effect noticed in the electrolysis of bismuth solutions with a platinum cathode.

A solution containing 0.2777 gram of bismuth in 12 cc., with 0.5 cc. of concentrated sulphuric acid, was electrolyzed with a

current of 4 amperes and 5 volts. Consecutive experiments showed that 0.2777, 0.2779, 0.2770, 0.2773 and 0.2767 gram of metal was precipitated in twelve minutes. The liquid removed from each of these deposits gave no test for the metal upon examination. There was not a trace of anodic precipitation at the completion of any one of these experiments. In the earlier stages of the decompositions the peroxide appeared on the anode wire but rapidly redissolved. Smooth wire should be used for the anode. If its surface is rough, the deposit, if there be any, will disappear very slowly. The anode should rotate rapidly, so



Curve XI. Bismuth—3 amperes, 5-4 volts (0.5 cc. sulphuric acid).

that the mercury may take up the metal which is deposited quickly, as it often collects in a black mass beneath the anode.

As bismuth solutions generally contain considerable free nitric acid, 0.5 cc. of the latter was added to each of six experiments in which a current of from 3 to 4 amperes and 5 volts acted for twelve minutes, precipitating 0.2778, 0.2769, 0.2768, 0.2775, 0.2776 and 0.2772 gram of bismuth respectively, at the rate of

0.1305 gram of metal in one minute.
0.2274 gram of metal in three minutes.
0.2515 gram of metal in five minutes.
0.2732 gram of metal in eight minutes.
0.2751 gram of metal in ten minutes.
0.2775 gram of metal in twelve minutes.

From these results Curve X was constructed.

The substitution of sulphuric for nitric acid appears to make little difference in the rate of the precipitation as may be seen from the following figures:

In five minutes 0.2409 gram of bismuth was deposited.
In ten minutes 0.2764 gram of bismuth was deposited.
In fifteen minutes 0.2770 gram of bismuth was deposited.

These gave Curve XI.

Experiment.	Bismuth present. Gram.	Volume. cc.	Sulphuric acid. cc.	Current. Amperes.	Volts.	Time. Minutes.	Bismuth found. Gram.	Error. Gram.
1	0.2273	12	0.5	3	5	15	0.2777	+0.0004
2	0.2273	12	0.5	3–4	5	15	0.2779	+0.0006
3	0.2273	12	0.5	4	5	12	0.2770	+0.0003
4	0.2273	12	0.5	3	5.5	15	0.2773	.....
5	0.2273	12	0.5	3	5	15	0.2767	—0.0006
6	0.2273	11.5	0.5	3	5	15	0.2770	—0.0003
			Nitric acid. cc.					
7	0.2273	11.5	0.5	4	5	12	0.2778	+0.0005
8	0.2273	11.5	0.5	4	5.75	12	0.2769	—0.0004
9	0.2273	11.5	0.5	4	5	12	0.2768	—0.0005
10	0.2273	11.5	0.5	4	5	12	0.2775	+0.0002
11	0.2273	11.5	0.5	4	5	12	0.2776	+0.0003
12	0.2273	11.5	0.5	4	5	12	0.2772	—0.0001
13	0.2273	11.5	0.5	4	5	12	0.2772	—0.0001

The many determinations given in the present communication as well as in the one which preceded it demonstrate beyond question that metallic sulphates and nitrates may be successfully electrolyzed with the mercury cathode and the rotating anode, the results in all instances being as satisfactory as with stationary

electrodes, it being possible also to determine the acid radical poured off in the liquid after the completion of the decomposition.

In the first paper published, relating to the use of a mercury cathode, it was shown that if in electrolyzing metallic halides, *e. g.*, sodium chloride, barium bromide, cobalt chloride, etc., use was made of a silver anode, the halogens could be determined simultaneously with the metals. Naturally, it was wished to know whether upon rotating the anode in halide solutions the halogens might be as easily determined. Accordingly, a flat platinum spiral and a disk of platinum, coated with metallic silver, were used as rotating anodes. The halogens of the electrolyzed halides promptly combined with the silver and for a while constituted an adherent deposit of silver halide, but as the layer thickened it began, because of the rapid rotation, to detach itself and become suspended in the solution. A silver disk was substituted for the silver-coated platinum anode with a like result. A large platinum dish, silver-coated and made a stationary anode, was used along with a smaller inner dish coated with mercury and made a rotating cathode with no better results. The silver halide formed upon the anode was disturbed by the agitation of the electrolyte, not equally readily it is true, and fell away from its electrode. Whether a scheme can be devised to make this perfectly adherent so that the metals may be quickly determined as in the case of sulphates and nitrates remains to be seen. Apparently, there is no reason why it should not be realized. Unwilling to exclude metallic halides from the field of experimentation, the problem was to eliminate the bad effects of the escaping halogens, for these did come off copiously in the electrolysis of any metallic halide upon employing the high current densities used with sulphates and nitrates. They also attacked the rotating platinum anode energetically. Could these undesirable behaviors be eliminated? Might not a layer of some organic liquid, superimposed on the aqueous halide, take up the halogens liberated in the electrolysis? A solution of cadmium bromide was made the electrolyte; upon it were placed 10 cc. of anhydrous ether. The anode was made to rotate quite rapidly and the current passed. The ether absorbed the bromine very fully and nicely. The heat of decomposition, however, caused a too rapid volatilization of the solvent so that toluene and xylene were substituted, in the later experiments, for the ether.

Both liquids proved most successful. The platinum anode was weighed before and after numerous experiments. Its decrease in weight for the entire series of experiments did not exceed 0.5 mg., a difference in weight that might easily be due to something other than solution of the anode.

COBALT CHLORIDE.

Five cubic centimeters of solution, containing 0.1250 gram of cobalt, were covered with 10 cc. of pure toluene and electrolyzed with a current of from 2 to 4 amperes and 5 volts. The liquid was colorless in five minutes and the metal completely precipitated in seven minutes. A second cobalt chloride solution (=0.1050 gram of cobalt) gave 0.1050, 0.1049, 0.1052 and 0.1048 gram. On using xylene as the solvent, equally good results were obtained.

GOLD CHLORIDE.

The conditions prevailing were:

5 cc. gold chloride equal 0.1200 gram of gold.

Toluene, 10 cc.

Current, 2 to 3 amperes.

Volts, 10.

Time, five minutes.

Gold found, 0.1200, 0.1201 and 0.1198 gram.

Gold is precipitated very rapidly so that it is advisable that the current be not too strong. The perfectly satisfactory conditions were found to be those which have been mentioned at the opening of this paragraph. The gold chloride solution should not stand long in contact with the mercury cathode because metal soon begins to separate and is with difficulty absorbed by the mercury.

IRON CHLORIDE.

Here the conditions were:

5 cc. ferric chloride equal 0.1030 gram of iron.

Toluene, 10 cc.

Amperes, 2 to 4.

Volts, 9.

Time, twelve minutes.

Iron found: 0.1025, 0.1030, 0.1029 and 0.1031 gram respectively.

MERCURIC CHLORIDE.

This electrolyte also lent itself quite well to the method. Five cc. of the solution contained 0.2525 gram of mercury. On

placing the solution upon the mercury, a slight coating was produced. It proved a poor conductor for with a pressure of 10 volts a scarcely preceptible current was observed. Upon the liberation of acid the current rose to 1 ampere and then to 3 amperes, with the pressure falling to 7.5 volts. The mercury was completely precipitated in ten minutes. Conditions:

5 cc. solution equal 0.2525 gram of mercury.
Toluene, 10 cc.
Current, 1 to 3 amperes.
Volts, 10 to 7.5.
Time, ten minutes.
Mercury found: 0.2524, 0.2525, 0.2524 gram.

TIN CHLORIDE.

Stannous chloride was dissolved in just enough hydrochloric acid to prevent the formation of any oxychloride. When the solution was too concentrated the tin was deposited so rapidly that it was not immediately incorporated with the mercury, and particles of it floated around in the electrolyte and in the layer of toluene. For this reason the electrolyte was diluted. The conditions giving satisfactory results were:

I.

5 cc. stannous chloride equal 0.0800 gram of tin.
Toluene, 10 cc.
Amperes, 2 to 3.
Volts, 7 to 6.
Time, 10 minutes.
Tin found, 0.0798, 0.0806 and 0.0802 gram

II.

10 cc. stannous chloride equal 0.1600 gram of tin.
Toluene, 10 cc.
Amperes, 2 to 3.
Volts, 7 to 6.
Time, 15 minutes.
Tin found, 0.1595 and 0.1600 gram.

CADMIUM BROMIDE.

This solution was so prepared that 5 cc. of it contained 0.2212 gram of metal. After the addition of 10 cc. of toluene, the liquid was electrolyzed with a current of 2 amperes and 5 volts. The

toluene became red in color but later changed to yellow. The odor of bromine was not detected. In ten minutes 0.2215 gram of metal was precipitated. The aqueous solution gave no test for it.

These examples will suffice to show that by using toluene, metallic chlorides can be electrolyzed with the mercury cathode and rotating anode, applying high currents and high pressure. It was not thought necessary to include other halides. Just what the action of the halogen was could only be determined by fractional distillation of the several portions of toluene which had been used in the various decompositions. This was done. There remained, after expelling the unattacked toluene, a portion which boiled at about 162–164° C., corresponding in this particular to a chlortoluene. Before we could, however, ascertain which one of the possible chlorinated products it really was there appeared in the *Journal of the Chemical Society* (London), **87**, 1034, a contribution upon "Studies in Chlorination," in which hydrochloric acid was electrolyzed under a layer of boiling toluene. The products were shown to be *o*- and *p*-chlortoluene, which were subsequently oxidized to *o*- and *p*-chlorbenzoic acids. The chlorinated body obtained by us was presumably a mixture of *o*- and *p*-chlortoluene. The purpose of the study being rather the electrolysis of metallic chlorides and not the action of electrolytic chlorine, further work in this direction was discontinued. Our study seems, however, to be a confirmation of the observation to which reference has just been made. Whether metallic chlorides would be preferable to hydrochloric acid for chlorinations of this description must be decided by others, as it is not our intention to develop this line of research.

At various times in this laboratory, since the introduction of the mercury cathode, separations have been made of iron from uranium, aluminium, thorium, lanthanum, praseodymium, neodymium, cerium and zirconium. They were most satisfactory. It remained to ascertain whether they would prove to be as good if they were conducted with the high currents and high voltage possible with the rotating anode. The nitrate or sulphate of each of the metals was tried first alone to discover whether it was at all affected. As this proved that not one of the metals mentioned in the preceding paragraphs was precipitated, the separations were begun and conducted as shown in the following sections:

IRON FROM URANIUM.

Uranyl sulphate. Gram.	Iron present. Gram.	Volume of solution. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.2	0.1777	7	2	3–5	7–5	15	0.1777	.....
0.1	0.1777	6	2	2–5	7–5	15	0.1772	—0.0005
0.2	0.1777	7	3	2.5–5	7–5	15	0.1769	—0.0008
0.2	0.1777	7	2	2.5–3.5	7–5	15	0.1775	—0.0002

IRON FROM ALUMINIUM.

Aluminium sulphate. Gram.	Iron present. Gram.	Volume of solution. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.2	0.1777	7	2	2–5	9–7	15	0.1777	.....
0.2	0.1777	7	0	2–4	9–7	15	0.1782	+0.0005
0.2	0.1777	7	2	2–5	9–7	15	0.1781	+0.0004
0.3	0.1777	8	2	2–4.5	7–6	15	0.1782	+0.0005

IRON FROM THORIUM.

Thorium nitrate. Gram.	Iron present. Gram.	Volume. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.2	0.1777	7	2	2–4	7–6	15	0.1777	.....
0.2	0.1777	7	2	3–5	6–5	15	0.1777	.....
0.3	0.1777	8	2	3–4	7–5	15	0.1777	.....
0.2	0.1777	7	2	3–4	7–5	15	0.1776	—0.0001

IRON FROM LANTHANUM.

Lanthanum sulphate. Gram.	Iron present. Gram.	Volume. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.2	0.1220	10	2	2–4	8–6	15	0.1221	+0.0001
0.15	0.1220	10	2	2–4	8–6	15	0.1226	+0.0006
0.25	0.1220	10	2	2–4	8–6	15	0.1226	+0.0006

IRON FROM PRASEODYMIUM.

Praseodymium sulphate. Gram.	Iron present. Gram.	Volume. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.25	0.1235	7	2	2–4	8–5	20	0.1240	+0.0005
0.3	0.1235	8	2	3–5	9–6	20	0.1234	—0.0001
0.3	0.1235	8	2	2–4	8–5	20	0.1229	—0.0006
0.25	0.1235	7	2	2–4	8–5	20	0.1230	—0.0005

IRON FROM NEODYMIUM.

Neodymium sulphate. Gram.	Iron present. Gram.	Volume. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.16	0.1235	7	2	3–4	7–5	20	0.1242	+0.0007
0.24	0.1235	8	2	3–5	9–5	20	0.1236	+0.0001
0.24	0.1235	8	2	3–5	9–7	20	0.1237	+0.0002
0.16	0.1235	7	2	3–5	9–5	20	0.1237	+0.0002

IRON FROM CERIUM.

Cerium sulphate. Gram.	Iron present. Gram.	Volume. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.12	0.1235	8	2	2–4	9–6	20	0.1237	+0.0002
0.24	0.1235	9	2	2–4	9–6	20	0.1236	+0.0001
0.36	0.1235	10	0	2–5	10–7	25	0.1230	—0.0005

IRON FROM ZIRCONIUM.

Zirconium sulphate. Gram.	Iron present. Gram.	Volume. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.2	0.1235	7	0	2–4	7–5	20	0.1238	+0.0003
0.3	0.1235	8	1	2–4	7–5	20	0.1230	—0.0005
0.5	0.1235	10	2	2–5	6–5	25	0.1238	+0.0003

UNIVERSITY OF PENNSYLVANIA.

THE USE OF AMMONIUM PERSULPHATE IN THE DETERMINATION OF CHROMIUM IN STEEL.[1]

By Harry Edward Walters.

Received October 24, 1905.

Ammonium persulphate is used as a reagent for oxidizing chromium in steel in a method described by F. Ibbottson and R. Howden.[2] After oxidation the chromium is precipitated as lead chromate, filtered and determined volumetrically.

The writer has been using a method for some time in which the same salt is used, advantage being taken of the fact that in the presence of sufficient silver nitrate both the chromium and manganese are completely oxidized and can be determined volumetrically without previous precipitation. The method as outlined is applicable for ordinary chrome steels but not for tungsten or molybdenum steels, as some of these steels contain a carbide of chromium insoluble in sulphuric acid. This difficulty can be overcome by filtering the insoluble carbide, burning and fusing with a small amount of sodium carbonate and adding to the main solution. This, however, would prolong the operation but would still be an advantage over the methods now in use.

METHOD.

Weigh 1.25 grams of the sample into a No. 3 Griffin beaker, add 35 cc. dilute sulphuric acid (1:5), warm until the sample is in solution and add a small amount of ammonium persulphate to oxidize the iron and carbonaceous matter; dilute to 100 cc. and add 40 cc. silver nitrate solution (0.16 gram of the salt), now add an excess of ammonium persulphate (5 to 7 grams) and heat to boiling. Boil about five minutes to destroy excess of persulphate, cool and transfer to a 500-cc. calibrated flask, dilute to mark with water and mix thoroughly.

Pour 100 cc. (0.25 gram) into a 100-cc. calibrated flask; the remaining 400 cc. (1 gram) are transferred to a beaker, a measured volume of ferrous sulphate added and the excess titrated with a standard solution of permanganate until a pink color is obtained.

The number of cubic centimeters of the permanganate solu-

[1] Read before the Pittsburg Section, October 19, 1905.

[2] *Chem. News*, **90**, 320.

tion used, subtracted from the number required for the volume of ferrous sulphate added, will give the volume of permanganate used by the chromium and manganese.

The contents of the 100-cc. calibrated flask are transferred to a porcelain dish and titrated with a standard solution of sodium arsenite until the color is bright yellow. The number of cubic centimeters of the arsenite solution used, multiplied by the value of the solution in manganese, will give the amount of manganese present.

The volume of permanganate used by the chromium is found by calculating the amount of manganese found to the equivalent number of cubic centimeters of the permanganate solution and subtracting this number from the volume of the permanganate used by the chromium and manganese. The number of cubic centimeters found to be used, multiplied by the value of the permanganate in chromium, will give the amount of chromium present.[1]

REAGENTS.

Sulphuric Acid.—A mixture of one part concentrated acid and five parts water.

Silver Nitrate.—Four grams of the salt are dissolved in one liter of water.

Ammonium Persulphate.—The salt should be slightly moist.[2]

Sodium Arsenite.—The solution is prepared as recommended by Blair.[3] The solution is standardized with a chrome steel of known manganese content so that the direct reading will give the per cent. of manganese. Mixtures of pure chromium and manganese solution may also be used.

[1] EXAMPLE.—Let us assume that the chromium value of each cubic centimeter of the permanganate solution equals 0.001 gram and the manganese value 0.000633 gram; now if 50 cc. of the ferrous sulphate solution equals 49 cc. of the permanganate solution and the sample after oxidation and addition of 50 cc. of the ferrous sulphate solution requires 13 cc. of the permanganate solution, then 49 cc. minus 13 cc. equals 36 cc. or amount used by chromium and manganese.

If the sample should show 0.38 per cent. manganese by the arsenite titration, then 0.0238 divided by 0.000633 equals 6 or the number of cubic centimeters of permanganate solution equivalent to the per cent. of manganese found.

36 cc. minus 6 cc. equals 30 cc. × 0.001 gram equals 0.03 gram or 3 per cent. chromium.

[2] The dry salt, or one which has been dried at 120°, sometimes gives a good reaction, but at other times we have failed to secure satisfactory results, while good results have always been obtained with the moistened salt. Others have had the same experience. Such a difference seems, on the face of it, absurd, and this statement is made only as an empirical fact which has no apparent reason.

[3] "Chemical Analysis of Iron," fifth edition, p. 121.

Permanganate Solution.—The solution is made by dissolving 1.82 grams of pure potassium permanganate in 1 liter of water.

Ferrous Sulphate Solution.—The solution is made by dissolving 22.5 grams ferrous ammonium sulphate in water, adding 50 cc. strong sulphuric acid and diluting to 1 liter.

It is unnecessary to have this exactly equal the permanganate solution as a constant volume is used and the solution loses in strength. It is only necessary to find the volume of permanganate equivalent to the volume of ferrous sulphate used and this should be done every day.

The permanganate may be standardized by getting the iron value or by the use of a pure chromium salt. If the solution is standardized against iron the chromium value is found by the equation

167.7 : 52.1 :: iron value : x equals chromium value, and the manganese value by the equation

279.5 : 55 :: iron value : x equals manganese value.

If the solution is standardized with a pure chromium salt the manganese value is obtained by the equation

260.5 : 165 :: chromium value : x equals manganese value.

REMARKS.

In case the samples should run high in chromium the ferrous sulphate solution could be made stronger.

The permanganate solution should be allowed to stand several days before standardizing.

In case an appreciable amount of vanadium is present in a sample it will be necessary to determine the manganese by the bismuthate or Ford's method.

In using the method for tungsten steels some tungstic acid separates, but this does not seriously interfere with the titration.

The following results were obtained on some chrome steels and pure solutions of iron, chromium and manganese.

Number.	Chromium taken. Per cent.	Found. Per cent.	Manganese taken. Per cent.	Found. Per cent.
1	4.00	3.98	0.08	0.09
2	4.80	4.82	0.40	0.40
3	1.56	1.53	0.24	0.23
4	3.60	3.57	0.80	0.81
5	5.10	5.12	0.50	0.49
6	8.00	8.03	0.32	0.32

Steels.	Chlorate method. Chromium.	Chlorate method. Manganese.	Persulphate method. Chromium.	Persulphate method. Manganese.
1	1.50	0.35	1.51	0.36
2	2.88	.....	2.85	0.14
Tungsten	3.50	0.12	3.49	0.13
Molybdenum	5.69	0.81	5.71	0.83

I wish to acknowledge my indebtedness to Mr. T. D. Rodgers of this laboratory for the careful manner in which he has carried out these experiments.

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REVIEW.

SOME RECENT WORK IN ORGANIC CHEMISTY.

BY LAUDER W. JONES.

Received October 30, 1905.

A review of the progress of organic chemistry must, of necessity, be a partial one. The greater part must be left untold. In preparing the following survey of the articles published by foreign investigators during the year 1904, I have chosen a few of the many interesting articles, and have been compelled, for lack of space, to exclude many which deserve mention. I hope that the ones which I have selected may be of general interest to those who are familiar with the methods and theories of organic chemistry.

During the year 1904, Grignard's reaction has been applied in a great variety of new syntheses, and seems to be at the beginning, instead of at the end, of its usefulness. Gomberg's triphenylmethyl is still an unsolved riddle. The investigations of Fischer and of Curtius which have led to the building up of so many complex polypeptides, are giving us quite substantial assurance of future success in the synthesis of natural proteins. The study of quadrivalent oxygen derivatives has been continued, and has led to the preparation of many interesting oxonium compounds. The use of powdered nickel in the presence of hydrogen at temperatures above 100° for the purpose of reduction seems to be a method of great promise which may be applied for the reduction of many classes of organic substances. On the whole, the year has given us nothing which is strikingly new, but much that is of interest and importance.

Hydrocarbons.—Some interesting results have been obtained by the slow combustion of certain hydrocarbons. Bone and Wheeler (*J. Chem. Soc.*, **83**, 1074 (1903)), in a previous article, showed that methane gave first formaldehyde and water, and,

finally, carbon dioxide, carbon monoxide and water. No methyl alcohol could be detected.

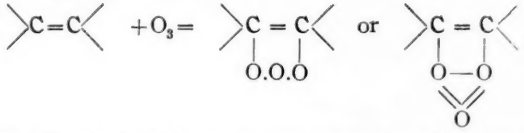
In a recent paper, Bone and Stockings (*J. Chem. Soc.*, 85, 693–727) describe the products formed by the slow combustion of ethane at temperatures ranging from 250–500°, and at increased and diminished pressures. They observe several stages in the oxidation; first, acetaldehyde and water; second, formaldehyde, carbon monoxide and water; third, carbon monoxide, carbon dioxide and water. Methane and hydrogen are secondary products which result from the decomposition of acetaldehyde and formaldehyde.

$$CH_3O.H \rightarrow CH_4 + CO$$
$$CH_2O \rightarrow H_2 + CO$$

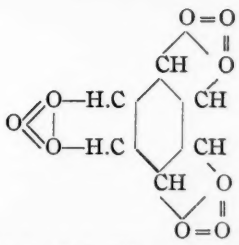
No ethyl alcohol could be detected.

Bone and Drugman (*Proc. Chem. Soc.*, **20,** 127–128), however, have observed that ozonized air (2.5 per cent.) at 100°, acts upon ethane, and yields, in addition to acetaldehyde and formaldehyde, traces of ethyl alcohol. It seems, therefore, that ethyl alcohol is the primary oxidation product of ethane. In a later article, Bone and Wheeler (*J. Chem. Soc.*, **85,** 1637–63) have presented their results with ethylene. The chief product is formaldehyde, accompanied by carbon monoxide, carbon dioxide and water.

Harries has continued his interesting experiments with ozone and organic compounds. The previous articles (*Ber.*, **36,** 1933, 2998, 3001, 3658) dealt with the action of ozone upon aldehydes, alcohols, iodobenzene, iodosobenzene and unsaturated compounds. He found that the double bond in unsaturated molecules was attacked, and the molecules were broken and oxidized by parts to aldehydes or ketones. He has recently discovered that ozone behaves in a different manner in non-dissociating solvents; ozone is absorbed by the double bond with the formation of compounds which Harries calls ozonides.

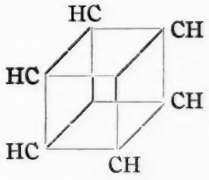


Such ozonides yield, with water, two molecules of ketone and one of hydrogen peroxide. Harries (*Ber.*, **37,** 2708) also studied the action of ozone upon caoutchouc, and succeeded in breaking the molecule into significant parts, through the intermediate formation of an ozonide. By an analysis of the ozobenzene prepared first by Renaud (*C. R.*, **120,** 1177), Harries and Weiss (*Ber.*, **37,** 3431–33) have shown that the formula $C_6H_6O_6$ is incorrect, and must be replaced by $C_6H_6O_9$. It is, therefore, benzene triozonide, and is formed by the addition of three molecules of ozone to benzene.



Pure dry benzene is treated with ozonized oxygen for one or two hours at a temperature of 5–10°. Ozobenzene is precipitated as a white, amorphous mass, which detonates when treated with warm water. By careful treatment with water, it is changed into glyoxal, CHO—CHO.

König (*Chem. Ztg.*, **29**, 30) suggests the cube as a possible space formula for benzene.



Sabatier and Mailhe (*C. R.*, **138**, 248–49) have succeeded in reducing many aromatic halogen compounds to the corresponding hydrocarbons, without, at the same time, adding hydrogen to the ring. This is accomplished by passing halogen compounds, mixed with an excess of hydrogen, over reduced nickel heated to a temperature of 270°. If several halogen atoms are present, they are replaced one after the other, not simultaneously. The presence of methyl or hydroxyl groups makes the replacement easier; amino groups facilitate it still more. Thus chlorbenzene gave benzene; chlornitrobenzene gave aniline hydrochloride. It is a singular fact that the replacement of bromine is not so easy as that of chlorine, while iodine is the hardest of all to replace.

In a second paper (*C. R.*, **138**, 407), the same authors try to extend the reaction to aliphatic halogen compounds, but without the same success, because of the dissociation of the halogen compounds at about 250°. Methyl iodide, however, gave chiefly methane, with some ethylene.

In a similar way, Darzens (*C. R.*, **139**, 868–70) reduces aromatic ketones at 190–195° to corresponding hydrocarbons.

$$C_6H_5.CO.R + 2H_2 = C_6H_5CH_2.R + H_2O$$

Thus acetophenone gave ethylbenzene; *p*-cresyl ketone gave

p-methylethylbenzene; benzylacetone gave *n*-butylbenzene. In the last case, the reduction occurs, even though the carbonyl group is not bound directly to the benzene ring.

Godchot (*C. R.*, **139,** 604–6), by means of the method just described, reduces anthracene at 250° to tetrahydroanthracene, $C_{14}H_{14}$, and at 200° to octohydroanthracene.

Fontana and Perkin (*Elec. Chem. Ztschr.*, **11,** 99–105) oxidize anthracene to anthraquinone by passing an electric current through a solution of anthracene in acetone, to which dilute sulphuric acid and cerium sulphate have been added.

Luther and Weigert (*Sitzungsber. Kgl. Pr. Akad.*, 1904, 828–39) have found that the change of anthracene to dianthracene in the sunlight, which was observed in solution by Fritzsche, also occurs in the solid and in the vapor forms of anthracene. The reaction is a reversible one.

$$\text{Anthracene} \underset{\text{In the dark}}{\overset{\text{In the light}}{\rightleftharpoons}} \text{Dianthracene}$$

The authors have studied it qualitatively and quantitatively.

Thiele and Balhom (*Ber.*, **37,** 1463–70) describe several interesting hydrocarbons called by them quinonoid hydrocarbons. In the course of experiments made with the object of preparing *p*-xylylene, $H_2C=C_6H_4=CH_2$, they obtained polymeric bodies of the same composition. By treating tetraphenyl-*p*-xylylene bromide, $C_6H_4(CBr(C_6H_5)_2)_2$, with metallic silver in the presence of benzene, they obtained tetraphenyl-*p*-xylylene, $(C_6H_5)_2C=C_6H_4=C(C_6H_5)_2$, a solid which crystallizes in red needles and melts at 239–40°. The solution is orange colored and fluorescent, and is soon decolorized by light.

Optically active benzene hydrocarbons were prepared by Klages and Sautter (*Ber.*, **37,** 649–55) by means of Grignard's reaction. They allowed benzaldehyde to act upon active amyl iodide in the presence of metallic magnesium and ether. The product obtained was treated in the usual way with dilute sulphuric acid. The chief substance formed was hexylenebenzene, $C_6H_5.CH=CH.CH(CH_3)C_2H_5$, with some of the carbinol $C_6H_5CH(OH).CH_2CH(CH_3)C_2H_5$. Hexylenebenzene is optically active, $[\alpha]_D^{15°}=+50.3°$. It may be reduced by the action of sodium upon an alcoholic solution; optically active hexylbenzene is obtained as a liquid which boils at 220° (757 mm.) and gives a value $[\alpha]_D^{14.5°}=+17.20°$. Hexylbenzene is not changed into a racemic form by six hours' heating with alcoholic potassium hydroxide at 160°.

The study of triphenylmethyl, $((C_6H_5)_3C)_2$(?), has led to no definite decision concerning the true constitution of this interesting substance. The experimental evidence (Gomberg: This Journal, **22,** 757; **25,** 317; *Ber.*, **33,** 3150; **34,** 2776; **35,** 1822, 2397, 3914;

36, 376, 3928; **37,** 1626) seems to point to the transient existence of triphenylmethyl as a univalent radical, which, in the presence of certain catalyzers, passes into a bimolecular form, distinct from the so-called hexaphenylethane. In the bimolecular state, it combines readily as an unsaturated compound with halogens to form triphenylmethyl halides. Gomberg (*Ber.*, **37,** 2033), by the action of zinc turnings upon triphenylmethyl chloride in benzene, or better still in acetone, has obtained triphenylmethyl in the form of beautiful, colorless crystals, which melt between 145° and 147°. A molecular weight determination by the freezing-point method shows that the molecule has become double. Solutions have a yellow color which Gomberg believes to be caused by the presence of the ion $(C_6H_5)_3C$. The experiments of Walden (*Ber.*, **35,** 2018) show that triphenylmethyl, triphenylcarbinol, triphenylmethyl chloride, when dissolved in liquid sulphur dioxide, are conductors and dissociated, thus bearing out the analogy of triphenylmethyl to a univalent group with base-forming properties.

Attempts to explain away the trivalent carbon have not been successful heretofore. (Norris and Sanders: *Am. Chem. J.*, **25,** 54, 117; **29,** 129; Kehrmann: *Ber.*, **34,** 3815; **35,** 622; Heintschel, *Ber.*, **36,** 320). Tschitschibabin (*Ber.*, **37,** 4709) proposed recently that triphenylmethyl is, in reality, hexaphenylethane. He points out that the so-called hexaphenylethane of Ullmann and Borsum (*Ber.*, **35,** 2877) is diphenylmethyltetraphenylmethane, $(C_6H_5)_3C.C_6H_4.CH.(C_6H_5)_2$, and not hexaphenylethane which is unknown, unless it is identical with triphenylmethyl. Gomberg, however, still maintains that his compound contains trivalent carbon, and accounts for its bimolecular condition by the assumption of associated molecules which, he says, occur in other cases, *e. g.*, the nitriles, the organic acids, etc.

Halogen Compounds.—Konowaloff (*J. Russ. Phys. Chem. Soc.*, **36,** 220–223) studied the action of dilute nitric acid upon halogen compounds, especially $(CH_3)_2CH.CH_2Cl$, $(CH_3)_2CHBr$, $(CH_3)_2CCl.C_2H_5$, and $(CH_3)_3CBr$. Thus, isobutyl chloride gave a nitro halogen compound $(CH_3)_2C(NO_2).CH_2Cl$. He found that saturated halogen compounds are more readily attacked by nitric acid than the corresponding paraffine hydrocarbons. Primary and secondary halogen derivatives yield nitro compounds with halogen in the molecule; tertiary (not aromatic) compounds yield halogen acids and unsaturated substances which may or may not be nitrated.

Halleman and Beekman (*Rec.*, **23,** 225–56; 257–64) prepare fluorbenzene, and certain substituted fluorbenzenes, by the action of concentrated hydrofluoric acid upon diazonium sulphates.

The behavior of aromatic halogen compounds towards copper, heated to temperatures ranging from 210 to 250°, has been studied quite thoroughly by Ullmann (*Ann. Chem.* (Liebig), **332,**

3881) and others associated with him. In this manner, C_6H_5I gave diphenyl to the extent of 82 per cent., while Fittig's method yields only 5 per cent. The same difference is observed in other cases. Copper could not be replaced with advantage by other metals. By this method, *o*-iodotoluene gave 2,2′-dimethyldiphenyl; *β*-iodonaphthalene gave 2,2′-dinaphthyl. The same method was applied with success to iodo derivatives of sulphonic acids, nitro and amino compounds, and many others.

OXYGEN COMPOUNDS.

Alcohols, Ethers, Phenols.—Grignard's reaction has been employed in a number of ways to prepare alcohols. Thus, Grignard (*C. R.*, **138,** 152–154) prepared the compounds RCO.OMgX in the usual way by acting upon the organo-magnesium halide with carbon dioxide. With a second molecule, R′MgX, these derivatives are changed into substances of the form $RR.'C(OMgX)_2$. A third molecule of the magnesium compound, R′MgX, reacts as follows:

$$RR'C(OMgX)_2 + R'MgX = RR'_2COMgX + (MgX)_2O.$$

This final product is decomposed by dilute sulphuric acid, with the formation of a tertiary alcohol. Grignard prepared in this way diethylisoamylcarbinol, isobutylisoamylcarbinol, phenyldiethylcarbinol, ethyldiphenylcarbinol.

Fallenberg (*Ber.*, **37,** 3578–81) allowed organo-metallic compounds to act upon mesityl oxide and phorone. With care, he succeeded in obtaining a tertiary alcohol by the action of methylmagnesium iodide upon mesityl oxide; it had the following structure: 2,4-dimethylpentene(3)ol(2), $(CH_3)_2C:CH.C(CH_3)_2OH$, and boiled at 46° (14 mm.). From phorone, he prepared 2,4,6-trimethylpentadiën (2.5)ol(4), $(CH_3)_2C:CH.C(CH_3)(OH)CH:C(CH_3)_2$.

The reduction of acid amides, especially in the case of the higher amides, furnishes a new and successful method of obtaining the corresponding alcohols. Bouveault and Blanc (*C. R.*, **138,** 152–54) carry out this reduction by allowing metallic sodium to act upon an alcoholic solution of the amide.

$$R.CO.NH_2 + 4Na + 4C_2H_5OH = RCH_2OH + 4NaOC_2H_5.$$

Some amine is formed, especially in the case of the lower amides. Caproic, pelargonic, and phenylacetic amides were reduced to the corresponding alcohols, with yields varying from 25 to 30 per cent. Scheuble and Loebl (*Monats. für Chem.*, **25,** 341–53, 1081–1105) substitute amyl alcohol for ethyl alcohol, and prepare many of the higher alcohols from the amides.

The method of Sabatier and Senderens was applied by Brunel (*C. R.*, **137,** 1268–69) to phenol, cresol, thymol, and carvacrol. By means of nickel and hydrogen, at temperatures between 100° and 200°, these compounds were reduced to the hexahydro alcohols. Phenol, at 170–175°, gave nearly the

theoretical amount of cyclohexanol, a liquid boiling at 160–161°. Thymol gave hexahydrothymol, $C_{10}H_{19}OH$, a liquid with a mint odor; it is stereoisomeric with menthol.

The behavior of halogen ethers towards organo-magnesium derivatives is studied by Hamonet (*C. R.*, **138,** 813–14). He used ethyl-, phenyl- and benzylmagnesium bromides, and allowed these to act upon the halogen ethers,

$$CH_3.O.CH_2Br \text{ and } C_5H_{11}.O.CH_2Br.$$

$$R.O.CH_2Br + RMgBr = R.O.CH_2R + MgBr_2.$$

In this way, he prepared amylpropyl ether, benzylmethyl ether and others.

Alizarindimethyl ether was prepared by Graebe (*Ber.*, **38,** 152–53) by changing alizarin into desoxyalizarin, methylating this with dimethyl sulphate in alkaline solution, and oxidizing the resulting product with sodium chromate in acetic acid solution. The ether crystallizes in golden yellow needles.

Aldehydes and Ketones.—Investigations made by Henriet (*C. R.*, **138,** 203–5) show that the atmosphere contains a small amount of formic acid, and, in addition, some formaldehyde. He estimated the formaldehyde to be between $^1/_{100,000}$ and $^5/_{100,000}$ by passing air over mercuric oxide heated to 250°, and collecting the carbon dioxide in potash bulbs; allowance was made for the carbon dioxide previously present in the air.

Several articles by Leyewetz and Gibello (*C. R.*, **138,** 1225–27), Korber (*Pharm. Ztg.*, **49,** 608), Litterscheid and Thimme (*Ann. Chem.* (Liebig), **334,** 1) deal with the known polymeric forms of formaldehyde, and describe the preparation of many new ones.

When α-hydroxy acids are heated, they yield first lactides. Blaise (*C. R.*, **138,** 697) finds that these lactides, upon distillation, lose carbon monoxide and some carbon dioxide, and are converted into aldehydes with one less carbon atom than the α-hydroxy acid. Thus: α-hydroxycaproic acid gave *n*-pentanal; α-hydroxynonylic acid gave *n*-octanal; α-hydroxypalmitic acid gave *n*-pentadecanal. This method furnishes a means of transition from acids C_n to acids C_{n-1}.

Grignard's reaction has been used, directly or indirectly, in the preparation of aldehydes and ketones by several new methods.

Galleman and Maffezzoli, Bouveault and others use ethyl formate with organo-magnesium compounds to obtain aldehydes. The yield is poor. Tschitschibabin (*Ber.*, **37,** 186–188: Also Bodroux: *C. R.*, **138,** 92–94) found that much better results could be secured by using orthoformic esters in the usual manner.

$$HC(OR)_3 + R'MgI = R'CH(OR)_2 + ROMgI.$$

These acetals may be hydrolyzed with dilute acids, and the aldehydes obtained. Thus, C_2H_5MgI, with orthoformic ethyl ester, gave a yield of 25 per cent. of the acetal $CH_3CH.C(OC_2H_5)_2$.

Béhal and Sommelet (*C. R.*, **138,** 89–92) employ a new method to prepare aldehydes of the forms $R_2CH.CO.H$ and $RR'CH.CO.H$. They heat α-glycol ethers, $RC(OH).CH_2OX$ or $RR'C(OH).CH_2.O.X$, in which X may be an alkyl or an aryl radical, with anhydrous oxalic acid.

$$2RR'C(OH).CH_2.O.X + C_2H_2O_4 = 2RR'CH.CO.H + C_2O_4X_2 + 2H_2O.$$

The desired α-glycol ethers are obtained from ethyl ethoxyacetate by the action of organo-magnesium compounds. Many aldehydes were prepared in this way.

Acetylene aldehydes are synthesized by Moureu and Delange (*C. R.*, **138,** 1339–41) by treating acetylene hydrocarbons in ether solution with organo-magnesium derivatives, and an excess of ethyl orthoformate. The reaction is completed by heat, and the product is treated with dilute sulphuric acid. Acetals of acetylene aldehydes result; these may be changed into the aldehydes. Amylpropiolic acetal, $C_5H_{11}C:C.CH(OC_2H_5)_2$, hexylpropiolic acetal, $C_8H_{13}C:C.CH(OC_2H_5)_2$ and phenylpropiolic acetal, $C_3H_5C:C.CH(OC_2H_5)_2$ are some of the acetals formed by this method.

Grignard's reaction has been used in numerous instances (Acree: *Ber.*, **37,** 616, 625, 2753; Hell and Stockmayer: *Ber.*, **37,** 225; Hell and Bauer: *Ber.*, **37,** 230, 453, 1429; Klages and Heilmann: *Ber.*, **37,** 1447) to change aldehydes and ketones of the aromatic series into secondary and tertiary alcohols which may, in some cases, lose a molecule of water to give unsaturated compounds.

Acids and Acid Derivatives.—An interesting reaction is described by Rengade (*C. R.*, **138,** 629–31). Sodium ammonium, $NaNH_3$, or potassium ammonium, KNH_3, react with carbon dioxide, at temperatures below —50°, exclusively in one direction, with the formation of a carbamate,

$$CO_2 + KNH_3 = NH_2—C\begin{matrix}O\\ \diagdown\\ OK\end{matrix} + H.$$

At somewhat higher temperatures (—35° to —25° for $NaNH_3$ and —10° to —5° for KNH_3), the free hydrogen reduces the carbamate partially to formate. This suggests the method employed by Moissan, in which carbon dioxide is reduced by means of sodium hydride, NaH, to formate.

Thioformic acid is prepared according to Auger (*C. R.*, **139,** 798) by saponifying phenyl formate with sodium sulphhydrate. Sodium thioformate, HCO.SNa, is obtained as white hygroscopic needles. If this salt is decomposed by formic acid (not hydrochloric) in the cold, and the product is distilled under diminished pressure, thioformic acid, H.CO.SH, may be collected in a receiver surrounded by methyl chloride. It is found to be a

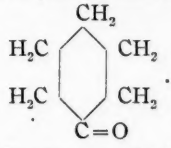
liquid which soon loses hydrogen sulphide and polymerizes to a white amorphous mass.

A method of characterizing fatty acids is suggested by Locquin (*C. R.*, **138,** 1274–76). It consists in preparing the semicarbazones of acetol fatty acid esters as follows: One gram molecule of the acid to be identified is treated, in ether solution, with the calculated amount of sodium, and then with monochloracetone.

$$RCO.ONa + ClCH_2CO.CH_3 = RCO.O.CH_2.CO.CH_3 + NaCl.$$

These acetol esters are then converted into semicarbazones which have definite melting-points.

Braun (*Ber.*, **37,** 3588–91) describes a new synthesis of pimelic acid. By treatment of benzoylpiperidine with phosphorus pentachloride or pentabromide, a mixture of benzonitrile and pentamethylene dihalogen is obtained. By the action of potassium cyanide, the pentamethylene compound is converted into $N{:}\ C(CH_2)_5C{:}\ N$, which, upon hydrolysis, yields normal pimelic acid. If the calcium salt of pimelic acid is heated, it yields



This series of changes affords a method of changing the imide group in piperidine to the carbonyl group.

Blaise and Gault (*C. R.*, **139,** 137–39) have found that formaldehyde condenses with two molecules of ethyl oxalate in the presence of piperidine and yields a compound,

$$CO.OC_2H_5CO.CH.(COOC_2H_5)CH_2CH.(COOC_2H_5).CO.COOC_2H_5.$$

By hydrolysis with dilute hydrochloric acid, this yields dioxypimelic acid, $COOHCO.(CH_2)_3CO.COOH$, a crystalline solid, which, by loss of water, is changed to pyrandicarbonic acid,

$$COOHC{:}CH.CH_2CH{:}C{-}O{-}COOH.$$

Many esters of fatty acids are secured by a new method proposed by Tschitschibabin (*Ber.*, **38,** 561–66). He applies Grignard's reaction to the neutral esters of carbonic acid. The reaction may proceed in three stages as follows:

I. $CO(OC_2H_5)_2 + RMgX = RC(OC_2H_5)_2O.Mg.X.$

II. $RC(OC_2H_5)_2OMgX + RMgX = R_2C(OC_2H_5)OMgX + C_2H_5O.MgX.$

III. $R_2C(OC_2H_5)OMgX + RMgX = R_3C.O.MgX + C_2H_5OMgX.$

If the reaction product is decomposed by dilute sulphuric acid after the first stage, an acid ester will result; if it is treated after the second stage, a ketone will be formed; after the third stage, a

tertiary alcohol will be obtained. With care, it is possible to realize the first process, and obtain a yield of 80 per cent. of ester. If orthocarbonic esters are used, orthoesters of fatty acids result.

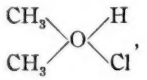
Marckwald (*Ber.*, **37,** 349–54) announces the synthesis of *l*-valeric acid, and considers that he has accomplished a true asymmetric synthesis. This he does by preparing the acid brucine salt of methylethylmalonic acid. By fractional crystallization, the less soluble form separates. When this brucine salt was heated to 170°, carbon dioxide was lost, and the brucine salt of valeric acid remained. With dilute sulphuric acid, this residue gave *l*-valeric acid, $[\alpha]_D = -1.7°$. This value corresponds to about 10 per cent. of *l*-valeric acid. Cohen and Patterson (*Ber.*, **37,** 1012–14) do not believe this synthesis is a real "asymmetric synthesis," such as Fischer, Cohen and Whiteley, Kipping and others have tried to effect, since it depends, they say, upon the separation of two enantiomorphous ions, already present in solution, by the formation of the salt of an active base. They consider the method to be identical with the one used by Pasteur.

Marckwald (*Ber.*, **37,** 1368–70), in reply, defines an asymmetric synthesis as one in which an optically active body results from a symmetrically constituted body, through the intermediate use of optically active substances, but without any analytical process. He considers the formation of *l*-valeric acid to be totally unlike the preparation of active malic acid from racemic acid, since the tartaric acid necessary must be prepared from racemic acid by an analytical process, *viz.*, by splitting according to Pasteur's method. He asserts that enantiomorphous ions are excluded, since methylethylmalonic acid reacts with brucine in chloroform or ether, non-dissociating solvents, and yields the acid brucine salt.

The structure of the lecithin molecule is determined by Willstätter and Lüdeke (*Ber.*, **37,** 3753–58). They find that free glycerolphosphoric acid, $CH_2OH.CH_2OH.CH_2O.PO_3OH$, is optically active, which determines the position of the phosphoric acid group.

Coehn and Jahn (*Ber.*, **37,** 2836–42) find that carbonic acid may be reduced to formic acid by means of the electric current, if a solution of sodium bicarbonate and potassium sulphate is chosen as the electrolyte. When a current of low density is used and carbon dioxide is conducted through the solution, formic acid is obtained. Even a pure water solution of carbonic acid gives a small amount of formic acid.

Oxonium Compounds.—The discovery of the hydrochloride of dimethyl ether,



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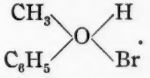
by Friedel (*Bull. Soc. Chim.*, **24,** 160) in 1875 may be considered as the starting-point in the chemistry of quadrivalent oxygen. In 1877, van't Hoff (*Ansichten u. die Org. Chem.*, p. 62) proposed that the compounds of quadrivalent oxygen might possess basic properties. Since that time, the evidence (Dale and Schorlemmer: *Ann. Chem.* (Liebig), **196,** 84; Classen and Ponder: *Ann. Chem.* (Liebig), **223,** 142; Wallach: *Ann. Chem.* (Liebig), **246,** 181; Perkin: *J. Chem. Soc.*, **69,** 1439) in favor of basic quadrivalent oxygen compounds has gradually accumulated.

Collie and Tickle, in 1896 (*J. Chem. Soc.*, **59,** 619), rejected the old method of considering these derivatives as "molecular combinations," and decided to explain them as basic compounds of quadrivalent oxygen. They studied especially dimethylpyrone. Baeyer and Villiger (*Ber.*, **34,** 2677) have contributed very important evidence. They found that alcohols, ethers, aldehydes, ketones, acids and esters all form crystalline compounds with acids, especially with hydroferrocyanic and hydroferricyanic acids. The evidence gained by applying physico-chemical methods (Walden: *Ber.*, **34,** 4185; Lacken: *Ber.*, **35,** p. 212; Cohen: *Ber.*, **35,** 2673; Collie and Tickle: *J. Chem. Soc.*, **85,** 971; Willstätter: *Ber.*, **38,** 1461) of investigation has settled the question in favor of basic quadrivalent oxygen compounds.

Recently, Archibald and McIntosh (*Proc. Chem. Soc.*, **20,** 139) have studied the action of liquid halogen acids upon acetone, ethyl ether, ethyl alcohol and other similar compounds. They find that hydrobromic, hydrochloric and hydriodic acids all form crystalline compounds which have melting-points ranging between —120° and —9°. By the action of liquid hydrobromic acid upon anisol, they obtain an oxonium compound,



This substance must contain an asymmetric oxygen atom.

McIntosh (*Proc. Chem. Soc.*, **21,** 64–5) allowed chlorine and bromine to act upon certain alcohols and ethers, acetone, acetaldehyde and ethyl acetate at low temperatures. Crystalline compounds resulted. Thus, $CH_3OH.Br_2$, which melts at —51°, and $(CH_3)_2OBr_2$, which melts at —68°, were obtained.

Cohen and Galecliff (*Proc. Chem. Soc.*, **20,** 194–96) find that ether, when shaken with dilute nitric acid, combines with it to form a compound which may be obtained as an explosive oil by drying the ether and evaporating it. An analysis of this oil gave the composition $(C_2H_5)_2OHNO_3$. Propyl ether combines in the same way with nitric acid to yield $(C_3H_7)_2O,HNO_3$.

Carbohydrates.—Morrell and Croft (*J. Chem. Soc.*, **75,** 786; **77,** 1219; **81,** 666; **83,** 1284–92) have continued their study of the action of ferrous salts and hydrogen peroxide upon carbohydrates.

They find that frequently, in addition to the osone, other products result by the splitting of the carbohydrate. Thus, glucose and *d*-fructose, with four molecules of hydrogen peroxide, give oxalic acid, glycolic acid, glyoxalic acid, and trihydroxybutyric acid. In a more recent paper, Morrell and Bellars (*Chem News*, **90**, 158–159; British Assoc. Rept., 1904) describe crystalline substances formed by the action of guanidine upon osones, CN_3H_5, $C_6H_{10}O_6$, C_2H_6O. Glucose and maltose form addition products with guanidine.

Ofner (*Ber.*, **37**, 3362–63) has studied the action of methylphenylhydrazine upon sugars.

Leyewetz and Gibello (*C. R.*, **138**, 150–152) obtain formose and glycerose by the action of sodium sulphite upon trioxymethylene.

Bau (*Z. ver. Rubenzucker Ind.*, 1904, pp. 481–521) has isolated crystalline melebiose, and finds it to be a solid melting at 84–85°. The liquid which remains after the fermentation of meletriose is treated with barium hydroxide, and the barium compound which is precipitated is treated with dilute sulphuric acid. By precipitation with alcohol and ether, melebiose, $C_{12}H_{22}O_{11}+2H_2O$, was obtained.

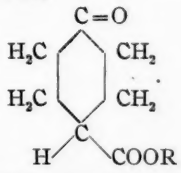
Bertrand (*Ann. Chim. Phys.* [8], **3**, 181–288) presents a complete survey of his fascinating studies in connection with the sorbose bacterium, which, in so singular a manner, is capable of oxidizing many polyatomic alcohols and sugars. In the case of polyatomic alcohols, he finds that the group =CH(OH) is changed to the carbonyl group. Thus, glycerol is changed to dihydroxyacetone, sorbitol to sorbose, mannitol to levulose. Aldoses yield by oxidation the corresponding monobasic acids which may be oxidized in turn to ketone acids, if they contain an oxidizable secondary alcohol group. Thus, gluconic acid gave, in the presence of the sorbose bacterium, oxygluconic acid. Recently, Bertrand has found that sorbose may be reduced by sodium amalgam in acid solution to a mixture of *d*-sorbitol and *d*-iditol. Dihydroxyacetone, contrary to the report of Piloty and Emmerling, is fermentable with difficulty. The reducible ketoses give no characteristic oxidation product, but are slowly destroyed by the sorbose bacterium.

Terpenes and Camphor Derivatives.—Brühl (*Ber.*, **37**, 746, 761, 2156, 2163, 2178, 2512, 3943) has made a study of the various halogen and acyl derivatives of camphorcarboxylic acid and of camphor itself.

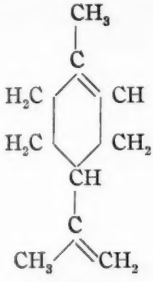
W. H. Perkin, Jr., (*Trans. Chem. Soc.*, **85**, 128) prepared synthetically *i*-α-campholactone, *i*-α-campholytic acid and β-campholytic acid.

The most important discovery in connection with the terpenes was made by W. H. Perkin, Jr. (*Trans. Chem. Soc.*, **85**, 654). He has worked out a complete synthesis of terpin hydrate, ter-

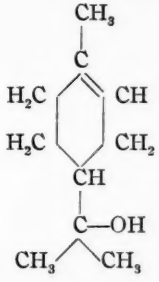
pineol, and dipentene. The starting material is the ethyl ester of δ-ketohexahydrobenzoic acid,



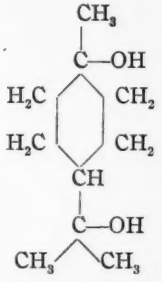
This ester is treated with magnesiummethyl iodide according to Grignard's reaction. The chief product is cis-δ-hydroxyhexahydro-*p*-toluic acid, $CH_2—CH_2—C(OH)(CH_3).CH_2—CH_2CHCOOH$, which, upon distillation, passes into the corresponding lactone. This lactone with concentrated hydrobromic acid is changed to δ-bromhexahydro-*p*-toluic acid, which, by digestion with pyridine or sodium carbonate, gives Δ^3-tetrahydro-*p*-toluic acid; when the ester of this acid is treated with magnesiummethyl iodide, it gives *i*-terpineol. This yields dipentene when it is treated with potassium disulphate, and terpin hydrate, when acted upon by dilute sulphuric acid. These relations are represented by the following formulae:



Dipentene.



Terpineol.



Terpin hydrate.

NITROGEN COMPOUNDS.

An interesting method of preparing normal sodium diazotate is recorded by Bamberger (*Ber.*, **37,** 629–30). It consists in treating nitrobenzene with sodium amide

$$C_6H_5NO_2 + NaNH_2 = C_6H_5N_2ONa + H_2O.$$

The yield is very small.

Sabatier and Senderens (*C. R.*, **138,** 457–60; 257–59) reduce aniline by means of nickel and hydrogen at 190° to cyclohexylamine, $C_6H_{11}NH_2$,—a colorless liquid with a strong basic odor. At the same time, dicyclohexylamine and cyclohexylaniline are formed. In a similar manner, at 160–180°, both mono- and

dimethyl- and ethylaniline, are reduced to the corresponding hexahydro compounds.

Amino Acids.—Curtius and Müller (*Ber.*, **37,** 1261–79) present many new investigations connected with the diazo fatty acid esters. They have found that only α-amino acid esters can furnish diazo fatty acid esters; from β- and γ-amino acid esters, no diazo compound could be isolated; while α-β-diaminopropionic ethyl ester gave α-diazo-β-hydroxypropionic ethyl ester.

A new synthesis of *r*-leucine is described by Bouveault and Locquin (*Bull. Soc. Chim.* [3], **31,** 1180–83). By treating α-oximinoisobutylacetic ethyl ester with sodium amalgam, they obtained α-aminoisocaproic ethyl ester, and from this α-aminoisocaproic acid, which is identical with *r*-leucine. Aluminium amalgam gave better results than sodium amalgam.

Fischer (*Ber.*, **36,** 2982; **37,** 2486–2511; **37,** 2842–48; 3062–71; 3871–75) has published many very interesting articles on the synthesis of polypeptides. It is interesting to note that there is a great similarity between these artificial polypeptides and the natural peptones. This is especially true of the synthetic products which contain more than one amino acid group, that is, "mixed polypeptides." The ordinary reactions of peptones, such as the biuret test, precipitation by phosphotungstic acid, hydrolysis by trypsin, are presented by the artificial polypeptides. Fischer thinks that the building up of polypeptides is the most important step in the synthesis of peptones. It will be impossible to give a review of this extensive work. The general method of procedure by which the simple amino acids lead to dipeptides, tripeptides, tetrapeptides, etc., is as follows: A monohalogen or dihalogen acid chloride is allowed to act upon an amino acid in the presence of alkali. Thus, monochloracetyl chloride with glycine gives

$$CH_2Cl.CO.Cl + H_2N.CH_2.CO.OH = CH_2Cl.CO.NHCH_2.CO.OH + HCl.$$

If the resulting monochlor derivative is treated with aqueous ammonia, the chlorine atom is replaced by the amino group,

$$CH_2Cl.CO.NH.CH_2.COOH + NH_3 = CH_2(NH_2)CO.NH.CH_2.COOH + HCl.$$

The resulting compound is a dipeptide, glycylglycine. The same reaction may be repeated again and again. Fischer carried the reaction as far as the pentapeptide, tetraglycylglycine, $H_2N—CH_2.CO.(NH.CH_2.CO)_3NH.CH_2.COOH$. Various other di-, tri- and tetrapeptides were built up, by selecting other monohalogen or dihalogen acid chlorides, and other amino acids, such as leucine, alanine, tyrosine. Mixed polypeptides were formed by using different chlorides. Thus dileucylglycylglycine, a tetrapeptide, was prepared by Fischer.

Derivatives of α-pyrrolidinecarboxylic acid, called by Fischer

"prolin," are studied by Fischer and Suzuki (*Ber.*, **37,** 2842–48), and by Fischer and Abderhalden (*Ber.*, **37,** 3871–75). This substance is of importance because it is the only imino base found in proteins.

Dyes and Related Compounds.—Previous attempts to prepare quinone diimide by the reduction of quinone dichlorimide failed. Willstätter and Mayer (*Ber.*, **37,** 1494–1507) succeeded in preparing it by treating the quinone dichlorimide with hydrochloric acid in absolute ether solution. Chlorine is liberated, and the hydrochloride of quinone diimide is formed. With ammonia in ether solution this salt yields quinone diimide, a substance which crystallizes in bright yellow crystals which decompose at about 50–60°.

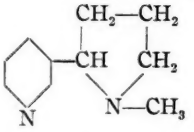
There is still no unanimity of opinion concerning the constitutions to be assigned to the triphenylmethane colors. Baeyer and Villiger have varied their opinion from time to time between the quinoid ammonium theory, and the theory of carbonium salts. In his last paper, Baeyer (*Ber.*, **38,** 569) considers that the quinoid structure is no longer tenable. He reverts to the carbonium theory, or a modified form of Rosenstiehl's (*C. R.*, **116,** 193) view. Many interesting suggestions concerning the structure of these compounds have been made by Hantzsch (*Ber.*, **37,** 3434), Von Braun (*Ber.*, **37,** 633, 2670), Vorländer and Siebert (*Ber.*, **37,** 3364), Straus (*Ber.*, **37,** 3277) and others.

Alkaloids.—The most important discovery of the year in connection with alkaloid chemistry, is the complete synthesis of nicotine. This was accomplished by Pictet and Rotschy (*Ber.*, **37,** 1225) in the following manner: In a previous article Pictet and Crepiéux (*Ber.*, **28,** 1904) describe the preparation of N-β-pyridylpyrrols by distilling β-aminopyridine mucate. When this substance is passed through a tube heated to redness, it is changed into the isomeric α,β-pyridylpyrrol. By the action of methyl iodide upon the potassium salt of this compound, α,β-pyridyl-N-methylpyrrol methyl iodide is formed. This is identical with the methyl iodide addition product of nicotyrine, which is obtained by the moderate oxidation of nicotine.

From this methyl iodide addition product, nicotyrine may be obtained by distilling it over heated calcium oxide. To change nicotyrine to nicotine, it requires the addition of four atoms of hydrogen. This could not be done directly, but was accomplished indirectly by preparing iodonicotyrine by the action of iodine and sodium hydroxide upon nicotyrine. The reduction of iodonicotyrine with tin and hydrochloric acid gave dihydronicotyrine. Finally, the perbromide of this dihydronicotyrine was reduced, and nicotine obtained. It appears to be identical with inactive nicotine.

Inactive nicotine was resolved into its active components by separating the crystallized tartrates into the *d*- and *l*-modifica-

tions. *l*-Nicotine, prepared synthetically, appears to be slightly different from natural *l*-nicotine. This synthesis establishes the correctness of the formula proposed by Pinner.



Through the investigations of Pauly (*Ber.*, **37,** 379), Jowett (*Trans. Chem. Soc.*, **85,** 192), and of Bertrand (*Ann. Institute Pasteur*, **18,** 672) the synthesis of adrenaline is fast approaching completion.

NEW BOOKS.

LANDOLT-BÖRNSTEIN PHYSIKALISCH-CHEMISCHE TABELLEN. Herausgegeben von DR. RICHARD BÖRNSTEIN und DR. WILHELM MEYERHOFFER. Berlin. Verlag von Julius Springer. 1905. Price, 36 marks.

The first edition of this indispensable work was published in 1883, the second in 1894, and the third has just appeared. In the first edition, 110 tables, occupying 246 pages, were prepared by six contributors. In 1894, there were 208 tables, occupying 560 pages, with seventeen contributors. The present edition contains 264 tables in 857 pages, with forty-seven contributors.

The increase in the variety of subjects tabulated is somewhat more than that suggested by the increase from 208 to 264 tables, for sometimes half a dozen or more tables in the second edition are counted as one in the present edition. So also, the 52 per cent. increase in the number of pages is much less than the actual increase in the amount of type set. The standard tables of the earlier edition have been given with type precisely equal in size to those used before, but some tables have been given in the more compact and convenient form in which six-place or seven-place logarithms are always printed, and some of the new matter is given in type which gives a fourth more lines on a page.

Like the first edition, the book gives tables for the reduction of the observations required by physical chemistry, and also a collection of the physical constants of this branch of chemistry, as well as a reference to the source of each. But the character of the book is so well known that detailed description of it is not required.

Some few subjects have called for no enlargement, like tables for reduction of volumes of gases to standard conditions. Such subjects as Elasticity, Capillarity, Viscosity, Thermal Expansion, Index of Refraction, each require about one-half more space than in the edition of 1894. Tables of Vapor-pressure, of Solubilities, and of Thermochemistry, each take about three times the former space. The most interesting point of difference between the second and third editions is seen in the tables on Solubilities. The seventeen pages entitled "Solubility of Salts.....in Water" in the edition of 1894, have, in the present edition, been transformed, by the results of studies guided by the phase rule, into sixty pages entitled "Equilibrium between Water and Inorganic Substances," and containing about forty diagrams exhibiting illustrative curves.

The tables of Electrical Conductivity have been much improved, but with some compression. Changes in other matters hardly call for specific mention.

This collection of tables would be indispensable even if the execution had left something to be desired. But the whole work of collection and selection, and editing, has obviously been performed with the thoroughness, the good judgment, and the skill and accuracy, which we had learned confidently to expect from its distinguished editors and from the contributors whom they should select.

In the first edition, Landolt's initial appeared at the bottom of not quite one-third of all the pages, and Börnstein's on nearly two-fifths. In the present edition, Landolt's name appears only in the title. The name of Börnstein, sometimes accompanied by another, appears on many more pages than before, and the third editor, Meyerhoffer, contributes about as many pages as did Landolt twenty years ago. Chemists feel towards the editors of 1883 and 1894, and will feel towards the editors of 1905, a gratitude which they would be glad of some opportunity to express, and congratulate them on the successful completion of a work so admirable in plan and so satisfactory in execution.

Good presswork and sound and durable paper do credit to the publisher; the binding is of doubtful durability.

EDWARD W. MORLEY.

RADIUM AND RADIOACTIVE SUBSTANCES. Their Application Especially to Medicine. By CHAS. BASKERVILLE, PH.D., Professor of Chemistry

and Director of the Laboratory, College of the City of New York, formerly of the University of North Carolina. Philadelphia: Williams, Brown and Earle. 1905. 164 pp. Price, $1.00.

As stated in the preface, the object of this book is "To fill a demand for an inexpensive non-mathematical work on the subject of radium and its application to medicine." The success which has attended the author's efforts is not perfectly apparent. The limited space which has been devoted to the discussion of the various topics has necessitated a briefness of treatment which is not always conducive to clearness of meaning, and the great number and variety of original papers to which reference is made have led to a condensation of material which not infrequently results in ambiguity. A lack of system in the presentation of the subject is apparent in a number of instances, as, for example, where separate sections are devoted to the discussion of actinium and "emanium" without any mention of their probable identity, and where the similarity between polonium and radio-tellurium is likewise disregarded.

The value of the book is much enhanced by the introduction of a generous series of references to individual papers which may possibly afford a convenient directory to some of those desiring to consult the original literature on the subject.

The chapters on the physiological action of radio-active substances and other therapeutic radiations cover about forty pages. It is stated in the preface that "The writer is not in a position to harmonize the contradictory evidence given in reputable medical journals as to the therapeutic uses of the salts of radium, consequently the observations have been impartially reported."

The general appearance of the volume is neat and attractive.

B. B. BOLTWOOD.

SPECTROSCOPY. By E. C. C. BALY, F.I.C., Lecturer on Spectroscopy, University College, London. London and New York: Longmans, Green & Co. 1905. Crown 8vo, vi + 568 pp. Cloth. Price, $2.80.

This volume is the latest of the series of Text-Books of Physical Chemistry, edited by Sir William Ramsay. It devotes 47 pages to a historical account, about 300 pages to prism, grating, and interferometer spectroscopic apparatus and methods of investigating the visible and invisible regions of spectra, with a chapter on efficiency of spectroscopes, and about 180 pages to the methods of production and nature of spectra, the Zeeman effect, series

relations, and changes of wave-length by pressure and by motion in the line of sight, concluding with a description of Rowland's ruling engine. Complete tables of wave-lengths have wisely been omitted, although the wave-lengths of the most important lines of the common elements are given in the text. Space is also saved by the omission of detailed descriptions and reproductions of spectra, real knowledge of which can be gained only by direct personal observation. The elementary optical theory of spectroscopic apparatus and the methods of adjustment and investigation are discussed with great thoroughness, with many valuable practical suggestions. For the purposes of the general student, it might have been better to have abbreviated the descriptions of the less commonly used apparatus and methods and to have given more space to such matters as the radiation of black bodies, Kirchhoff's law and "luminescence," changes in spectra produced by changes in physical conditions, and the bearing of recent ionic and electron theories on radiation phenomena, particularly on the origin of multiple spectra.

The book is clearly and concisely written and attractively printed, but contains some typographical errors.

There has long been need of a compendious text-book in spectroscopy, thoroughly up-to-date and giving a really adequate working knowledge of instruments and methods of research. This work very satisfactorily supplies the need, and will be warmly welcomed by all teachers of the subject.

PERCIVAL LEWIS.

ELEMENTS OF APPLIED MICROSCOPY. By CHARLES-EDWARD AMORY WINSLOW, Instructor in Industrial Microscopy and Sanitary Biology in the Massachusetts Institute of Technology. 12mo. 183 pp. 60 illustrations. New York: John Wiley & Sons. Price, $1.50.

This little book is intended for the beginner with the microscope. It meets a pedagogic need as a text in a course having for its object facility in manipulation of the microscope and acquaintance with the scope of its practical applications.

The first four chapters describe the function and manipulation of the principal parts and attachments of the modern compound microscope, and the general technique of microscopy. The remainder of the book—about 120 pages—is given to an interesting survey of the principal fields in which the microscope has been applied to practical affairs, *e. g.*, microscopy of starches,

foods, drugs and adulterants, textile fibers and paper; the microscope in medicine, sanitation, forensic cases, chemistry, petrography and metallography. Sixty figures elucidate the text.

The material is for the purpose of illustration and conservative suggestion rather than detailed description. The book contains but little original data and does not attempt to treat any single subject with completeness from the standpoint of the expert. A bibliography at the end of each chapter will be of use to the student stimulated to consult the more exhaustive works.

The book can be very helpful to beginning microscopy students of almost every class. ROBERT E. LYONS.

THE POLARISCOPE IN THE CHEMICAL LABORATORY. By GEORGE WILLIAM ROLFE. New York: The Macmillan Company. Price, $1.90.

At the present day no laboratory for ordinary research, commercial business, or teaching is considered complete without a good polariscope. There has long been need for a handbook less ponderous than Landolt's for the use of students and analysts. This work of Rolfe is intended to supply this want.

The author gives a short account of the fundamental principles of optical polariscopy. A brief history of the polariscope is given with a description of the ordinary types. The polariscope as a saccharimeter is next described with an account of the accuracy of saccharimetrical uses. The methods of installing and caring for a saccharimeter are given in some detail and are of great value. Apparatus which are used in connection with the polariscope are briefly described. Special forms of polariscopes also receive a separate chapter. The general principles of polarization of cane-sugar for commercial purposes are set forth and the ordinary errors attending the commercial use of the polariscope for the determination of cane-sugars are pointed out. The author is of the opinion that the sum of the errors of ordinary commercial work is practically zero, since some of them, such as the presence of lead precipitate, tend to increase the polarization, and others tend to diminish it, as for instance, polarization at temperatures above that at which the instrument is standardized. This observation could hardly be applied with justice to the ordinary polarization of sugars for dutiable purposes. The great bulk of these sugars are centrifugal sugars of the first crystallization of an average polarization of about 95. The lead precipitate in these sugars is extremely minute. They, however, are often

polarized at from 10° to 15° above the standard temperature of the instrument, thus introducing an error of from 0.3 to 0.5 per cent.

Usual methods of polarization where more than one optically active substance is present are described. The importance which the author attaches to errors caused by change in specific rotation of sucrose due to concentration would lead the reader to the opinion that such change is greater than that in specific rotation due to variation of temperature; such, however, is not the case.

A valuable chapter is that relating to the application of the polariscope in scientific research; this shows how the polariscope may be used in the study of some of the fundamental principles of physical chemistry. A valuable chapter is also contributed on the application of the polariscope to other bodies besides carbohydrates. A very interesting and practical part of the work is not indicated by the title; namely, pages 111 to 220 inclusive, which deals chiefly with technical subjects relating to sugar and starch manufacture, and the chemical methods for the determination of sugars and other carbohydrates.

The book as a whole will prove useful. It may be regarded as a reduction to practice of Landolt's work, to which have been added many practical suggestions derived from the large experience of the author. H. W. WILEY.

SEWERAGE AND SEWAGE PURIFICATION. By M. N. BAKER, PH.B., C.E. New York: D. Van Nostrand Company. 1905. Price, 50 cents.

This book is a second edition of No. 18 of the Van Nostrand Scientific Series which was published in 1895. The study of the past ten years has added decidedly to our knowledge of the bacterial changes that sewage undergoes as the decomposition of the organic matter that it contains proceeds. The ideal purification of sewage is accomplished when its noxious substances are completely changed into mineral substances and harmless gases. To do this as completely as possible and at an allowable cost is the aim of the sanitary engineer, and the studies of the past ten years have had this end in view.

Mr. Baker has had the opportunity to study, not only in this country but in England, the change in methods that has resulted from this study, and the portion of his book that treats of sewage purification, the last fifty-eight pages, has been almost entirely rewritten, and describes briefly but clearly the treatment of sewage by intermittent filtration beds, by septic tanks, by contact beds

and percolating filters. The first ninety-five pages of the book are devoted to sewerage and are practically a reprint of the same pages of the first edition. They treat of the health value of a sewerage system, preliminary reports and plans, cost and methods towns can employ for meeting the cost, and also details regarding construction, as main conduits, grades, man-holes, catch basins, storm overflows, depth and ventilation of sewers. The book is well written and gives a good general idea of the main points of a sewerage system and of sewage treatment. It can well be said to be one of the best of Van Nostrand's Scientific Series.

LEONARD P. KINNICUTT.

THE JOURNAL OF BIOLOGICAL CHEMISTRY. Edited by J. J. ABEL AND C. A. HERTER. Vol. I, No. 1. New York. 1905. Subscription price, $3.00 per volume.

It has long been recognized that a very considerable amount of excellent work in biological chemistry is done in this country which suggested the desirability of founding here a journal devoted to this growing specialty. Such a journal was announced some months ago and the first number has just been issued. It contains five articles, as follows: John J. Abel and R. DeM. Taveau: "On the Decomposition Products of Epinephrin Hydrate;" Reid Hunt: "The Influence of Thyroid Feeding upon Poisoning by Acetonitrile;" P. A. Levene: "The Cleavage Products of Proteoses;" Edward R. Posner and William J. Gies: "Is Protagon a Mechanical Mixture of Substances or a Definite Chemical Compound?" Frank P. Underhill: "Certain Aspects of Experimental Glycosuria."

On the title-page along with the names of the editors there are the names of twenty-two men as collaborators. This list of names is sufficient to guarantee the successful future of the journal, as far as contents, at any rate, are concerned. The general appearance of the new publication, which is printed on good paper with clear type, calls for distinct praise.

J. H. LONG.

JAHRBUCH DES VEREINS SPIRITUS-FABRIKANTEN IN DEUTSCHLAND, UND DES VEREINS DER STÄRKE-INTERESSENTEN IN DEUTSCHLAND. Fünften Jahrgang, 1905. Für der Schriftleitung verantwortlich, DR. G. HEINZELMANN. Berlin: Paul Parey. Price, M. 6.

As usual, this Jahrbuch is a true record of progress in the alcohol and starch industries of Germany, better known

in this country as the corn-products industries. It covers the proceedings of the two leading societies, in which are discussed the questions relating to culture of the potato, the sole source of starch and largely the source of alcohol in Germany, the preservation of the crop, the operations of manufacture both mechanical and chemical, and the work of the Gährungs-Institut in Berlin. It is distributed free to all members of the two societies named and to subscribers to the *Zeitschrift für Spiritus Industrie*. It is a work which should find place in the library of every one interested in either of the industries named. It is not possible to enter into details of the contents of this excellent Jahrbuch. It is sufficient to say that practically every step in the manufacture of starch and alcohol is intelligently discussed, beginning with the most excellent paper of Privy Councillor Delbrück on "Enzyme Action" and, including the report of Dr. Hanow upon questions which have arisen in the spirit distilleries, regarding pure yeast and grain distilleries, acetic acid manufacture and the manufacture of starch, that of P. Lindner and Dr. Henneberg on the exhibitions, fermentation methods, pure cultures, etc. Abstracts of papers on technical subjects published in the *Zeitschrift für Spiritus Industrie*, Jahrgang, 1904; answers to queries by Dr. Heinzelmann, the latter covering the use of potatoes, Jerusalem artichokes, and fecal matter as sources of alcohol in which he discusses all the stages of manufacture, and statistics of the industries by Dr. Lange and Dr. Behrend, all combine to make the Jahrbuch of exceptional value to agriculturists and spirit and starch technologists alike. For instance, the studies in potato culture and the results obtained are well worthy of the careful attention of our agriculturists; the technical uses of alcohol will interest those who would have tax-free alcohol in this country and should be carefully studied. According to the Jahrbuch, fecal matter as a source of alcohol must be abandoned. Like its predecessors, this Jahrbuch commands both interest and respect and is quite worthy of its very eminent authors. WILLIAM MCMURTRIE.

SUGAR AND THE SUGAR CANE. An elementary treatise on the agriculture of the sugar cane and on the manufacture of cane sugar. By NOEL DEERR. Published by Norman Rodger, Altrincham (Manchester). Price, 7s 6d net.

The object of the author in publishing this interesting book of 400 pages, as stated in his preface, "is to present in one con-

secutive whole a general view of the cane-sugar industry. As there is no recent work in English covering this ground, he hopes that this compilation may be of use to the English-speaking community connected with the cane-sugar industry." In compiling the information contained in this treatise, the author very modestly disclaims any great originality on his own part; nevertheless he has shown, on the whole, such good judgment in the difficult task of selection and arrangement of material that his publication will rank as one of the most valuable of recent contributions to the literature upon the subject. Contrary to the usual custom of writers upon sugar-cane, the author has not limited himself to the conditions and methods of any one cane-producing country, but has treated his subject from a general standpoint, as is evidenced by the wide range of books and journals consulted.

The first 8 chapters of the book deal with the general characteristics of the cane and its agricultural requirements. The cultivation, irrigation and fertilization of cane are fully discussed, as well as the methods of harvesting, transporting, and unloading.

Chapters 9 to 19 are given to the discussion of sugar-house work, special stress being laid upon the subjects of extraction, evaporation, and crystallization. The molasses and bagasse problems are also briefly treated.

Chapters 20 to 23 give directions for the chemical control of the sugar house with a description of methods of analysis. The author's omission, however, of Allihn's method for glucose—the standard method of sugar chemists in this country and Germany —must be regarded as a serious mistake. His criticism of the German process as being less accurate and convenient than the time-consuming "American (?) method" of Defren and O'Sullivan is hardly warranted.

The concluding chapter of the book upon "fermentation" will be of interest to those desiring information upon molasses distillation. The typography of the volume is, on the whole, good, and the text is well illustrated with numerous explanatory cuts and diagrams. The nine colored plates of several typical varieties of cane are an especially attractive feature. Louisiana readers will no doubt fail to recognize their so-called home canes, the Ribbon and Purple, under the names of Striped Tanna and Black Tanna. This, however, is only one of countless instances

of the confusion which has arisen in the nomenclature of canes, and the reader, after finishing Chapter III of Mr. Deerr's book, will readily agree with his verdict that the subject of classification "is in an almost hopeless state."

Those desiring a condensed treatise upon the agriculture and technology of the sugar-cane industry will find Deerr's "Sugar and the Sugar Cane" deserving of attention.

C. A. BROWNE, JR.

ECONOMIC GEOLOGY. A semi-quarterly journal devoted to geology as applied to mining and allied industries. Published by the Economic Geology Publishing Co., 41 N. Queen St., Lancaster, Pa. Price, 50 cents a copy, or $3.00 a year; foreign subscription, $3.75 a year.

This journal has been established to fill the long-felt want of a periodical in the English language devoted exclusively to the subjects named in the sub-title. It is the purpose of the founders to make this in every way a first-class medium for the publication of articles of scientific merit, excluding those which have to do with the engineering and commercial aspects of mining. That this high aim is likely to be fulfilled, the names of the editor and his associates give full assurance. These are: J. D. Irving, editor; Waldemar Lindgren, James F. Kemp, Frederick L. Ransome, Heinrich Ries, Marius R. Campbell, Charles K. Leith, associate editors. The first number appeared in October, with contributions by Messrs. Ransome, Kemp, Campbell, Lindgren and Keith of the editorial board, and E. C. Sullivan. Most if not all of these will be duly noticed in the pages of this Journal devoted to abstracts. W. F. HILLEBRAND.

CATALOGUE OF THE WARD-COONLEY COLLECTION OF METEORITES. By HENRY A. WARD, A.M., LL.D. Chicago, 1904. xii + 113 pp. Plates.

The Ward-Coonley collection, as all students of meteorites know, is deposited provisionally in the American Museum of Natural History, New York City. The falls represented numbered in the year of publication 603, thus making it in this respect the largest of the great collections. Following a preface and introduction, the catalogue proper is subdivided into sections covering Siderites, Siderolites, Aerolites, after which come lists of all known meteorites and their geographical distribution, a section on taxonomy, etc. The publication is worthy of the great collection which it represents. W. F. HILLEBRAND.

RECENT PUBLICATIONS.

ANALYSIS OF MILK AND MILK PRODUCTS. By H. Leffmann. Ed. 3, rev. Philadelphia: P. Blakiston Son & Co. 1905. 6+78 pp. $1.25.

ON THE QUANTITATIVE SEPARATION OF THE GLOBULINS OF HEMOLYTIC SERUM WITH SPECIAL REFERENCE TO THE CARBON DIOXIDE GROUP. By C. Quinan. Berkeley, Cal.: University of California Press. 1903. (1904). $0.05.

A TREATISE ON CHEMISTRY. Vol. I. NON-METALLIC ELEMENTS. New ed., rev. By Sir H. E. Roscoe. New York: Macmillan. 1905. 12+931 pp. $5.

A LABORATORY HAND-BOOK FOR THE ANALYSIS OF MILK, BUTTER, AND CHEESE. Ed. 2. By Jas. R. Evans. Troy: Arthur M. Allen. 1905. 60 pp. $1.25.

A SYSTEMATIC COURSE OF PRACTICAL ORGANIC CHEMISTRY. By L. G. Radcliffe and F. Sinnatt. New York: Longmans, Green & Co. 1905. 11+264 pp. $1.40.

PRODUCER GAS: THE PROPERTIES, MANUFACTURE AND USES OF GASEOUS FUEL. By A. H. Sexton. New York: Spon & Chamberlain. 1905. 225 pp. $4.00.

TRAITÉ DE CHIMIE APPLIQUÉE. T. 1. By C. Chabrié. Paris: Masson et Cie. 1905. 40+876 pp. 22 fr.

ANALYSE CHIMIQUE MINÉRALE, QUALITATIVE ET QUANTITATIVE. By E. Prost. Paris: Ch. Béranger. 1905. 12 fr. 50.

ZUR ERKENNTNIS DER KOLLOIDE. ÜBER IRREVERSIBLE HYDROSOLE U. ULTRAMIKROSKOPIE. By R. Zsigmondy. Jena: G. Fischer. 1905. 6+186 pp. 4 marks.

ANLEITUNG ZUR QUALTITATIVEN CHEMISCHEN ANALYSE. FÜR ANFÄNGER U. GEBÜ[illegible]ERE. Aufl. 4. By G. H. and Remigius C. Fresenius. 2te Bd. Braunschweig: F. Vieweg & Sohn. 1905. 16+872 pp. 18 marks.

PHYSIKALISCH-CHEMISCHE TABELLEN. Ed. 3. By R. Börnstein and W. Meyerhoffer. Berlin: Springer. 1905. 16+861 pp. 36 marks.

UEBER CHINOLINAZINE. By G. Wichern. Hamburg: W. Mauke Söhne. 1905. 1 mark.

LEAD POISONING IN EARTHENWARE AND CHINA WORKS. London: Wyman. 1905. $1^1/_2$ d.

CHEMISTRY BY OBSERVATION, EXPERIMENT, AND INDUCTION: A LABORATORY MANUAL FOR STUDENTS. By J. Iredelle D. Hinds. Second edition. New York: J. Wiley & Sons. 1905. 6+349 pp. $1.00.

OUTLINES OF PHYSIOLOGICAL CHEMISTRY. By S. P. Beebe. London: Macmillan. 1905. 6/6.

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THEORY AND PRACTICE OF PAINTING ON METAL. By Alvah Horton Sabin. New York: E. Smith & Co. 1905. 65 pp. (For free distribution.)

CHEMISTRY SIMPLIFIED: A COURSE OF LECTURES ON THE NON-METALS BASED UPON THE NATURAL EVOLUTION OF CHEMISTRY. By G. A. Koenig. Philadelphia: H. Carey Baird. 1905. 270 pp. $1.50.

A MANUAL OF ASSAYING: THE FIRE ASSAY OF GOLD, SILVER, AND LEAD, INCLUDING AMALGAMATION AND CHLORINATION TESTS. By Alfred Stanley Miller: Third edition revised and enlarged. New York: John Wiley & Sons. 1905. 8+148 pp. $1.00.

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ATOMIC WEIGHT OF CHLORINE: ATTEMPT TO DETERMINE EQUIVALENT OF CHLORINE BY DIRECT BURNING WITH HYDROGEN. By H. B. Dixon and E. C. Edgar. London: Dulau. 1905. 32 pp. 4/.

DECOMPOSITION OF WATER BY RADIUM. By W. Ramsay. London: Wesley. 1905. 3 pp. /6.

CEMENTS, LIMES, AND PLASTERS: THEIR MATERIALS, MANUFACTURE AND PROPERTIES. By Edwin C. Eckel. New York: John Wiley & Sons. 1905. 34+712 pp. $6.00.

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COKE: A TREATISE ON THE MANUFACTURE OF COKE AND OTHER PREPARED FUELS. By J. Fulton. Second edition. Scranton, Pa.: International Text-book Co. 1905. 14+497 pp. $5.00.

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